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Fortsetzung auf der III. Umschlagseite

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Automatic Coulometric Micro-Determination of Unsaturation with Kinetic Proof of Real Equivalence-Point

By

W. Walisch and M. R. F. Ashworth

(Received September 10, 1958)

Many procedures based on halogen addition, especially of bromine, have been described for the analysis of unsaturation of mixtures, and some of these have been adopted as standard methods for routine analyses. In the majority of procedures an excess of halogen reagent is used, the unreacted part of which is back titrated after a certain interval for reaction. In more recent years procedures of direct titration with halogen reagent have been worked out. For bromine reagent, a solution in a suitable solvent like carbon tetrachloride has been used, for example by *Braae*[1]; or the bromine is produced "in situ" from the more stable bromate/bromide mixture on titration into an acidified reaction mixture, as by *DuBois* and *Skoog*[2]. Coulometric generation and measurement of bromine, especially good for micro-determinations, has been introduced by *Bratzler* and *Kleemann*[3], *Leisey* and *Grutsch*[4], and *Miller* and *DeFord*[5].

The requirements of an accurate, general method are that the addition reaction proceeds to completion and that no other reactions occur which consume bromine. These requirements are usually fulfilled only to a limited degree and it is generally accepted that no method is both accurate and applicable to all types of olefinic compounds. Most methods aim at reasonable accuracy for limited classes of compounds, such as the standard methods for unsaturation in petroleum fractions. It has been shown for example in the work of *Unger*[6], who compared results for many pure olefines using 2 tentative standard methods and a modified *DuBois* and *Skoog* procedure, in which the Beckman "Aquameter" was used for automatic titration, that the requirements of complete addition and no side reactions were not fulfilled in the standard methods even

for a number of mono-olefinic hydrocarbons, usually regarded as the most favourable unsaturated compounds for determination by bromine addition.

One of us *(W.)* has recently undertaken kinetic investigations of the bromination of olefinic compounds[7,8]. These investigations were carried out under conditions where the reaction speed at any moment was found to be proportional to the bromine and to the olefine concentrations and evidently only addition occurred and no substitution. It was shown that even the olefinic hydrocarbons studied had speeds of bromination varying over a range of more than 10^4; that various reaction mechanisms may operate for other types of olefinic compounds depending on the nature and position of substituents in the molecule; and that changes in reaction conditions which accelerated the bromination of one type of compound, retarded that of another. These results further stress the difficulty of obtaining a method that is both accurate and general.

The apparatus developed for the kinetic investigations, using an automatic coulometric titration enables the microanalysis of unsaturation to be carried out and provides evidence about the above requirements, i. e., whether the addition is complete and if side reactions are occurring. It can further be used for analysis of certain mixtures of olefines. The present work describes some of these applications.

Principle of the Method

Since the apparatus has been described in detail elsewhere by one of us *(W.)*[7,9] only the principle is given here. It consists of a reaction vessel; a modified universal end-point indicator with automatic titration device (Commercial name "Titravit", see [10–12]), which functions on the polarovoltric principle; a coulometric system of electrolysis electrodes, current stabiliser and coupled stopwatch. The automatic switching on and off of the electrolysis corresponds to the bromine concentration in the reaction vessel falling below or exceeding, respectively, a pre-selected end-point value which can be chosen within wide limits ($1 \cdot 10^{-5}$ to $15 \cdot 10^{-5}$ Mol/litre in the present work). In a fast bromination, the reagent is consumed rapidly and its concentration in the reaction vessel will remain low. Titration will proceed practically in one uninterrupted run until at the end of reaction the pre-set end-point concentration of bromine is attained and electrolysis and the coupled stop-watch automatically stopped. With slower brominations, the first interruption will be before the equivalence point; electrolysis and reaction will then continue intermittently in ever-smaller bursts as the bromine is consumed and regenerated, until the equivalence point is reached. The stopwatch records the aggregate time of electrolysis. When the current is constant

and *Faraday*'s electrolysis law holds, the time of current flow is a measure of the amount of bromine generated.

There are three electrical requirements for accurate coulometric titration;

(a) constant electrolysis current,

(b) applicability of *Faraday*'s law,

(c) constant end-point bromine concentration.

These points are evidently wholly satisfied by the apparatus used. The stability of the electrolysis current was better than $\pm$ 0.2% even with voltage fluctuations of $\pm$ 10% and variations of resistance of the electrolytic cell of several 100%. As checked with pure arsenious oxide, *Faraday*'s law applied exactly under the conditions used. Changes of the end-point bromine concentration during titration were in general of the order of 10^{-7} Mol/litre and thus negligible even in ultramicro titration.

Results

The method gave evidence of the applicability of the two conditions mentioned in the introduction, namely, complete addition and absence of other reactions consuming bromine. Side reactions, like substitution, for example, would show themselves by a sensibly constant, slow bromination following the initial fast bromination. Under the conditions used in the present work, where the speed of bromination is proportional to the bromine concentration, an equilibrium addition reaction would be displaced by a change in the end-point bromine concentration, so that a different titration value would be found. None of the substances studied showed these effects under the reaction conditions employed.

1. Titration of Mono-Olefinic Compounds

Rapid addition reaction and suppression of possible disturbing side reactions like substitution were achieved by working in a solvent containing 10–40% water. As shown in previous kinetic measurements[7,8] the speed of bromination of mono-olefinic hydrocarbons and some other similarly behaving compounds is markedly increased through this water addition, whereas $\alpha\beta$-unsaturated carbonyl compounds (which probably have a different bromination mechanism, with induction period) then react negligibly. No readings were necessary during titration, which can be taken as completed when the time of current flow shows only insignificant further change.

Some results illustrating this are in Table I, as are the results with arsenious oxide, used as mentioned to show that the requirements of the electrolytic part of the method were fulfilled. A number of other unsaturated compounds were successfully titrated by this method,

including *n*-hexene, *n*-undecene, undecylenic acid, diisobutylene, cyclohexene, oleic acid and allyl alcohol. The last-named reacted inconveniently slowly so that titration lasted more than 30 minutes.

Table I

V = volume in ml of solution for analysis; I = electrolysis current in mA; c' = concentration of the solutions examined in gram equivalents/litre (equivalents to 1 Mol bromine); α_u' = theoretical time in seconds of current flow to equivalence of the amount of substance, given by $\alpha_u' = c' \cdot V \cdot (1.93 \cdot 10^5)/I$; α_u = time of current flow found (stopwatch reading) in seconds; α = time of current flow in seconds for reaction time t minutes

	V	I	α_u'	α	t	α_u	$(\alpha_u - \alpha_u')/\alpha_u'$
As_2O_3 0.004 Mol/litre	5	98.6	78.30			78.35	+ 0.1%
$c' = 0.008$	5	146.5	52.73			52.86	+ 0.2%
	5	200.0	38.63			38.57	— 0.1%
Aqueous Solution	5	299.2	25.83			25.92	+ 0.3%
n-Heptene	5	149.6	133.5	131.26	2	133.20	— 0.3%
$c' = 0.0207$				132.34	4		
				132.68	6		
				133.00	10		
Methanolic solution				133.20	15		
	5	203.8	98.0	97.62	5	98.10	+ 0.1%
				97.94	10		
				98.10	15		
2,6-Dimethylheptene-3	5	203.8	119.7	115.72	4	119.60	— 0.1%
$c' = 0.0253$				118.16	8		
				118.96	12		
				119.30	16		
Methanolic solution				119.60	22		
	5	203.8	119.7	119.28	15	119.60	— 0.1%
				119.60	23		
	5	203.8	119.7	119.20	15	119.50	— 0.2%
				119.50	20		
Elaidic acid	5	143.0	242.0	237.12	5	237.50	— 1.9%
$c' = 0.0359$				237.32	6		
Methanolic solution				237.50	10		
	5	143.0	242.0	237.22	6	237.40	— 1.9%
				237.40	10		
	10	143.0	484.0	476.46	11	476.64	— 1.5%
				476.64	14		

Briefly summarising, it is possible to classify the olefine compounds studied into 3 groups, according to ease of analysis under the conditions used. This is given below;

Structure of Compound (X = functional group)	*Analysis*
1. Olefine hydrocarbons and compounds containing C=C—C—CX, or where X is still further removed from the C=C bond	accurate and rapid determination
2. Compounds with the structure C=C—CX	determination often possible but reaction may be slow in some cases
3. Compounds with the structure C=CX	usually difficult and inaccurate determination (other reaction mechanism ?)

The reproducibilities are seen from the table to be better than $\pm$ 0.3% in all cases. The absolute accuracies, excepting elaidic acid, are of the same order. The small fluctuations are probably caused by errors in measurement of the volume of solution, which were checked to be in the region of $\pm$ 0.2%. Elaidic acid yielded an absolute value about 2% low, which is almost certainly due to impurities resistant to bromination. Negligible further bromination took place on longer standing and change in the pre-set end-point bromine concentration also caused no further bromine uptake.

2. Special Problems of Mixtures

Mixtures can be analysed when the olefine components are brominated at sufficiently different speeds. A rough rule can be given for the accuracy of analysis. The relative errors when the components are present in about equal amounts, are approximately the quotients of the reaction velocity constants.

1. *Marked difference in bromination speed ($> 5 \cdot 10^2$):* As mentioned earlier, addition of water to the methanolic reaction mixture reduces the bromination speed of the $\alpha\beta$-isomer of unsaturated carbonyl compounds sensibly to zero, whereas it raises that of the $\beta\gamma$-form by roughly a factor of 10 for 10% water. Some test mixtures of the isomers of mesityl oxide in different proportions were titrated in the presence of water and the proportions of $\beta\gamma$-isomer thus obtained were found to complement to 100% with fair accuracy the proportions of $\alpha\beta$-form determined by ultraviolet spectrophotometry. Similar behaviour was found for other $\alpha\beta$- and $\beta\gamma$-unsaturated carbonyl compounds, so that the proportion of $\beta\gamma$-form can probably be thus determined in many cases.

2. *Smaller difference in bromination speed:* Here, two procedures are possible, one determining the total and the faster reacting component;

the other, the total and the slower reacting component. The other component is then obtained by difference.

(a) *Total and faster reacting component:* The end-point bromine concentration and water content of the reaction mixture is chosen so that the faster reacting component reacts reasonably rapidly and the slower only insignificantly. $\alpha = f(t)$ is then measured until $\delta\alpha/\delta t$ is sensibly constant. This linear part is extrapolated to $t = 0$, giving the value α_a corresponding to the faster reacting component. Addition of water or raising the end-point bromine concentration now permits determination of α_u for the sum of both components (this sum α_u could be obtained by a longer wait under the original reaction conditions but the acceleration with water or more bromine usually saves considerable time).

(b) *Total and slower reacting component:* The reaction conditions are now selected so that the bromination in its slower stage allows kinetic measurements according to the well-known *Guggenheim* procedure for first-order reactions to be carried out. Where:

α = time of current flow for reaction time t,
α' = time of current flow for reaction time $(t + \varepsilon)$,
α_b = time of current flow to equivalence of the slower reacting component,
ε = fixed time interval of the *Guggenheim* procedure,
k = velocity constant of the reaction of this component,
C = a constant,

the following equations hold:

$$\log (\alpha' - \alpha) = \log C - k\,t,$$

$$C = \alpha_b\,(1 - 10^{-k\varepsilon})$$

(a more detailed derivation is given by one of us in a previous publication[7, 9]).

In the usual *Guggenheim* plot of $\log (\alpha' - \alpha)$ against t, k is given by the gradient and $\log C$ by the intercept for $t = 0$. Introduction of the values of k and C and that of ε into the second equation gives α_b and hence the amount of slower reacting component. α_u for both components together, the time of current flow to the end of reaction with both components, is usually obtained at the end of the *Guggenheim* plot; if desired, this end value can be obtained more quickly by reaction acceleration through addition of water.

Both procedures were tried on the diisobutylene mixture of 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2. 12.6 mg of the diisobutylene were taken and at 198 mA electrolysis current the calculated time of electrolysis was 110 seconds. Extrapolation of $\alpha = f(t)$ according to method (a) gave α_a for the faster reacting pentene-2 compound of 22.5 seconds. After addition of water, a total time of current flow for

bromination of both isomers of 110.4 seconds was found, agreeing excellently with the calculated value. The proportion of pentene-2 compound to pentene-1 compound was thus found to be about 1 : 4, in accordance with the usual value. Analysis by method (b), using the same weight of substance and electrolysis current gave α_b for the slower reacting form of 85–88 seconds, which again yields the approximate 1 : 4 ratio.

Experimental

Apparatus

A detailed description with diagrams has been given by one of us[7,9]. Some brief details are given here.

Reaction Vessel: This was cylindrical and double-walled to enable thermostatic control with a circulation pump. A plastic cover held the indicator electrodes; the tube carrying the stirrer; and the electrolysis anode and cathode, the latter being within a tube communicating with the main solution via a ground glass filter. The stirring speed was about 3000 r. p. m.

Indicator Part: This consisted of a modified Titravit. A direct potential difference, capable of being varied between 2 and 20 volts, was applied across a resistance of 0.8 megohm to the indicator electrodes. These were each of platinum wire, 15 mm long and 0.4 mm thick, fused into a double capillary. Changes in the polarisation voltage set up between the electrodes control the electrolysis current, via an amplifier and relay.

Current Stabiliser: The current stabiliser consists of 3 power amplifier tubes in parallel, the control grids of which are linked with the anode of a control pentode. The potential of the joined cathodes of the 3 power amplifier tubes depends, for a given cathode resistance (which can be varied at will within large limits in order to give different desired electrolysis currents) only on the value of the electrolysis current. As soon as this potential deviates from an opposed reference voltage given by a battery, this deviation and thus the change in electrolysis current is immediately and accurately compensated through the control pentode and the power amplifier tubes.

Stopwatch: From ZIVY, Paris, accurate to 0.02 seconds.

Chemicals

Methanol: This was distilled in a simple column after addition of a few drops of bromine in order to remove any unsaturated and bromine-sensitive impurities.

Sodium bromide: Prolabo R. P., Paris.

Methanolic sodium bromide: 0.2 Mol/litre.

Arsenious oxide: Prolabo R. P. pour analyses.

n-Heptene: Organico, Paris.
Dimethylheptene: Phillips Petroleum Co., U. S. A.
Elaidic Acid: BDH, England.
Diisobutylene: Eastman-Kodak, U. S. A.
Mesityl oxide: Touzart & Matignon, Paris.

Titration Procedure

About 50 ml sodium bromide solution was measured into the reaction vessel, and water added as needed for the particular experiment. The desired end-point bromine concentration was generated by electrolysis and the Titravit regulated to respond to this concentration and thus automatically switch the electrolysis current on or off depending on whether the bromine concentration in the reaction vessel was lower or higher than this critical value. The samples for analysis were then weighed into the reaction vessel, or, if in the form of solutions, pipetted. The desired electrolysis current was pre-regulated and switched on, simultaneously starting the coupled stopwatch. In the normal titration of mono-olefinic compounds, the titration was allowed to continue until the stopwatch came to rest or made only negligible further movement, this final value being taken as the titration electrolysis time. For the special problems of type 2., the time of current flow was read from the stopwatch at definite reaction time intervals.

Summary

A fully automatic coulometric method has been applied successfully to the determination of unsaturated compounds on the micro-scale. Results are quoted which show a reproducibility of $\pm$ 0.3% for mono-olefinic hydrocarbons. It is possible to control by means of a simple operation whether the addition reaction is complete and unaccompanied by side reactions. It has been shown that the concentrations of olefines in a mixture can be determined when their bromination speeds differ sufficiently from each other.

Zusammenfassung

Eine für kinetische Zwecke entwickelte vollautomatische, coulometrische Methode wurde mit Erfolg auf die „Bromtitration" ungesättigter Verbindungen im Mikromaßstab angewandt. Die angeführten Testuntersuchungen zeigen, daß bei monoolefinischen Kohlenwasserstoffen und ähnlichen Verbindungen die erreichbare Reproduzierbarkeit besser ist als $\pm$ 0,3%. Die Anordnung ermöglicht auf einfache Weise die Feststellung, ob die Addition vollständig abgelaufen ist und ob der Titrationswert nicht durch eine Nebenreaktion verfälscht wird. An Beispielen wird gezeigt, wie bei Gemischen olefinischer Verbindungen, die Bestandteile ausreichend verschiedener Reaktivität enthalten, die einzelnen Anteile nebeneinander bestimmt werden können.

Résumé

Les auteurs ont appliqué avec succès une méthode coulométrique entièrement automatique pour le dosage des composés non saturés à l'échelle microanalytique. Les résultats obtenus sont reproductibles à $\pm$ 0,3% près pour les hydrocarbures mono-oléfiniques. Une opération simple permet de contrôler que la réaction d'addition est complète et qu'elle n'est pas accompagnée par des réactions secondaires. Les auteurs ont montré également qu'il était possible de déterminer les concentrations de diverses oléfines dans un mélange lorsque leurs vitesses de fixation du brome diffèrent suffisamment les unes des autres.

References

[1] *B. Braae*, Analyt. Chemistry **21**, 1461 (1949).
[2] *H. D. DuBois* and *D. A. Skoog*, Analyt. Chemistry **20**, 624 (1948).
[3] *K. Bratzler* and *H. Kleemann*, Erdöl und Kohle **7**, 559 (1954).
[4] *F. A. Leisey* and *J. F. Grutsch*, Analyt. Chemistry **28**, 1553 (1956).
[5] *J. W. Miller* and *D. D. DeFord*, Analyt. Chemistry **29**, 475 (1957).
[6] *E. H. Unger*, Analyt. Chemistry **30**, 375 (1958).
[7] *W. Walisch*, Dissertation, University Saarbrücken. 1956.
[8] *W. Walisch* and *J. E. Dubois*, Chem. Ber. (in the press).
[9] *W. Walisch*, Annales Univ. Saraviensis **7**, 289 (1958).
[10] *J. E. Dubois* and *W. Walisch*, C. r. acad. sci., Paris **242**, 1161 (1956).
[11] *J. E. Dubois* and *W. Walisch*, C. r. acad. sci., Paris **242**, 1289 (1956).
[12] *W. Walisch*, Chim. analytique **39**, 63 (1957).

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A Turbidimetric Micromethod for Analysis of Tertiary Butyl Alcohol

By

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With 2 Figures

(Received November 28, 1958)

The Denigès reagent, a solution of mercuric sulphate in diluted sulphuric acid, is used in a well-known qualitative test for tertiary alcohols and some others which are readily dehydrated to olefines[1]. These latter are evidently first formed in the reaction and then yield insoluble yellowish, white or brown complexes with the reagent, usually of indefinite and variable composition, depending on the reaction conditions[2]. The test appears, however, not to have been much used as a basis for quantitative analysis. *Lindenberg*[3] has described a method for tertiary butyl alcohol, using reaction conditions in which it yields a precipitate of composition $C_4H_8(HgSO_4 \cdot HgO)_3$; the precipitate was separated, dissolved in excess standard hydrochloric acid and the unused acid back titrated.

In view of the sensitivity of the test for tertiary alcohols and of the paucity of analytical methods for these compounds, the possibility of a turbidimetric method for them has been examined in the present work. The effect of various factors such as the concentration of sulphuric acid and of mercury and the time of heating, has been studied. A boiling solution is used in the qualitative test and in the present quantitative study, temperatures of 95° and 100° have been used. Lower temperatures have not been tried because of the consequent disadvantage of too low reaction speeds.

Experimental

Reagents: Mercuric sulphate. 4 g mercuric oxide were dissolved in 50 ml approximately 6 *N* sulphuric acid and the solution diluted to 200 ml. The acid concentration of the solution was about 1.2 *N*.

Sulphuric acid. Solutions about 7 *N* and 18 *N*, with factors.

Tertiary butyl alcohol. 2.52 g were diluted to 1 litre and 5 ml of this solution further diluted to 1 litre. This second solution thus contained 12.6 μg/ml.

Procedure: Mixtures in various proportions of the 3 above solutions and water were prepared in test-tubes of similar optical properties. These were placed in a bath of hot or boiling water; at intervals the hot solutions were removed from the bath and their light absorption quickly measured with a photoelectric colorimeter (Electrosynthèse, using Filter 2 which is Ilford No. 622 with maximum transmission at about 460 nm). Results are expressed as optical density referring to that of the starting solution in the cold.

The water bath was opaque or the work carried out in artificial light or light of weak intensity.

Results

In accordance with the qualitative test, the solutions developed a yellow turbidity which in function of time reached a maximum and then decreased in intensity. (At low sulphuric acid concentrations, turbidity developed in the solution even in absence of the tertiary alcohol; this is probably due to hydrolysis of the mercuric sulphate and these lower acid concentrations were subsequently avoided.)

The effect of various factors studied is described below:

Concentration of the Sulphuric Acid

Up to a certain point, increase in acid concentration led to more intense turbidity with faster development followed by faster fall-off. Beyond this point, further increase resulted in less intense turbidity, ultimately inhibiting it completely, at least within the time of reaction studied (about 30–40 minutes). This inhibition is evidently not due to solution of the precipitate in the excess acid, because addition of further acid did not cause the precipitate to dissolve; moreover, partial neutralisation of a solution after heating with this higher, turbidity-inhibiting acid concentration, did not lead to turbidity formation.

An example in Table I illustrates the effect of variation of acid concentration.

Table I. Turbidity Development at Different Acid Concentrations
Temperature of bath = 95°
Concentration of Mercury = 2 g HgO/litre
Concentration of Tertiary Alcohol = 2.52 mg/litre

Acid Concentration	Optical Density after t Minutes				
	5	10	15	20	25
0.68 *N*	0.73	1.53	1.73	1.85	1.73
1.04 *N*	2.10	2.86	2.81	2.61	
1.40 *N*	2.06	2.70	2.65	2.46	
1.77 *N*	1.97	2.41	2.32	2.23	
2.13 *N*	1.03	1.89	1.87	1.42	
2.94 *N*	0.09	0.12	0.09		

In this example, as in others, the maximum turbidity was attained within a fairly narrow range of acid concentration. Some further data under various reaction conditions are in Table II.

Table II. Turbidity Development under Different Reaction Conditions

	°C	Alcohol Concentration mg/litre	Reagent Concentration HgO/litre	Normality of Acid for Maximum Turbidity	Optical Density of Maximum Turbidity
1	100	1.26	2.0	1.0–1.3	2.0–2.1
2	100	2.52	2.0	1.0–1.5	3.4–3.6
3	100	5.04	2.0	1.2–1.5	6.1–6.3
4	100	1.26	6.0	1.3–2.1	ca. 2.6
5	100	1.26	8.0	1.6–2.2	ca. 2.6
6	100	2.52	8.0	1.6–2.2	4.0–4.3
7	95	1.26	2.0	1.0–1.5	1.6–1.7
8	95	2.52	2.0	1.0–1.4	2.8–2.9
9	95	1.26	6.0	1.9–2.3	2.0–2.1
10	95	5.04	1.0	0.9–1.1	3.2–3.3

Concentration of Mercury

Increase in mercury concentration led to more intense turbidity and a more rapid development. From Table II, comparing lines 1, 4, and 5 or lines 2 and 6 or lines 7 and 9, it can be seen that the acid concentration for maximum turbidity was higher and extended over a wider range when more mercury was present.

Concentration of Tertiary Butyl Alcohol

Under otherwise constant reaction conditions, turbidity increased with increase in the alcohol concentration, as required for an eventual quantitative analytical method. Comparison of lines 1, 2, and 3 or of lines 7 and 8 in Table II show this and show further that this increase in alcohol concentration has no significant influence on the acid concentra-

tion needed for maximum turbidity. The development of turbidity was faster in solutions of higher alcohol concentration.

Temperature

The influence of temperature was not studied in detail, but comparison of lines 1, 2, and 4 with 7, 8, and 9 respectively, in Table II, shows that although the acid concentration for maximum turbidity was negligibly influenced, the 5° difference significantly changed the optical density.

Light

Daylight, especially sunlight, accelarated the decay of turbidity. Whereas in the dark or in light of low intensity the turbid solutions cleared ultimately when kept at 100° for several hours, in sunlight, however, they became clear in about a minute. Evidently there is no simple decomposition of the precipitate into isobutylene and regenerated mercury reagent, since a cleared solution did not become turbid on addition of further tertiary alcohol. Neither this effect, nor that of the inhibition of turbidity at higher acid concentration has been studied further in the present work.

Quantitative Determination of the Tertiary Alcohol

The best conditions for a quantitative method are those which yield a steep curve of optical density against concentration of alcohol and a flat curve of optical density against time, at least at the time of measuring the density. Evidently, conditions of high acid and mercury concentrations favour the former but not the latter. Trials were made with two mercury concentrations (2 and 8 g HgO/litre), each at two acid concentrations near the optimum for turbidity development. Some data are quoted in Table III:

Table III. Optical Densities after t Minutes
Temperature of bath = 100°

Alcohol Concentration, mg/litre	2 g HgO/litre				8 g HgO/litre			
	Sulphuric acid 1.32 *N*		Sulphuric acid 1.65 *N*		Sulphuric acid 1.65 *N*		Sulphuric acid 2.17 N	
	5 *t*	7.5 *t*	5 *t*	7.5 *t*	5 *t*	7.5 *t*	5 *t*	7.5 *t*
1.51	2.23	2.51	1.73	1.77	2.81	3.01	3.35	3.26
2.27	3.18	3.35	2.91	2.86	4.18	4.13	4.58	4.35
3.02	4.16	4.18	3.90	3.65	5.20	5.11	5.67	5.29
3.78	4.94	4.90	4.47	4.25	6.42	6.19	6.01	6.42
5.04	6.42	6.13	5.57	5.20				

In no case is the rate of change of optical density in the 5–7.5 minute region, so large that a reading a few seconds early or late would introduce significant error.

These and further data are plotted in Figs. 1 and 2:

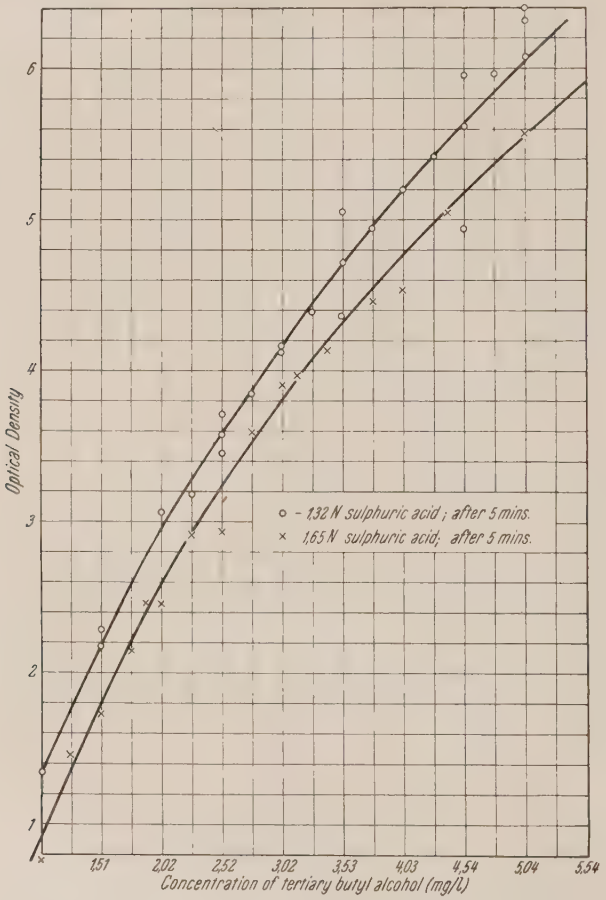

Fig. 1

The points lie on reasonably smooth curves. Occasional values show more marked deviations from the curves as is usually unavoidable in turbidimetric methods, but the use of duplicate or triplicate determinations would largely eliminate this source of error.

The curves of Fig. 2 are sensibly straight lines and are steeper than those of Fig. 1. Despite the higher speed of turbidity development in the Fig. 2 data, the points are no more scattered than in Fig. 1, so that the

conditions giving Fig. 2 can probably be recommended for a quantitative method to determine the concentration of very dilute aqueous solutions of tertiary butyl alcohol to within about 5% error. Turbidimetric methods

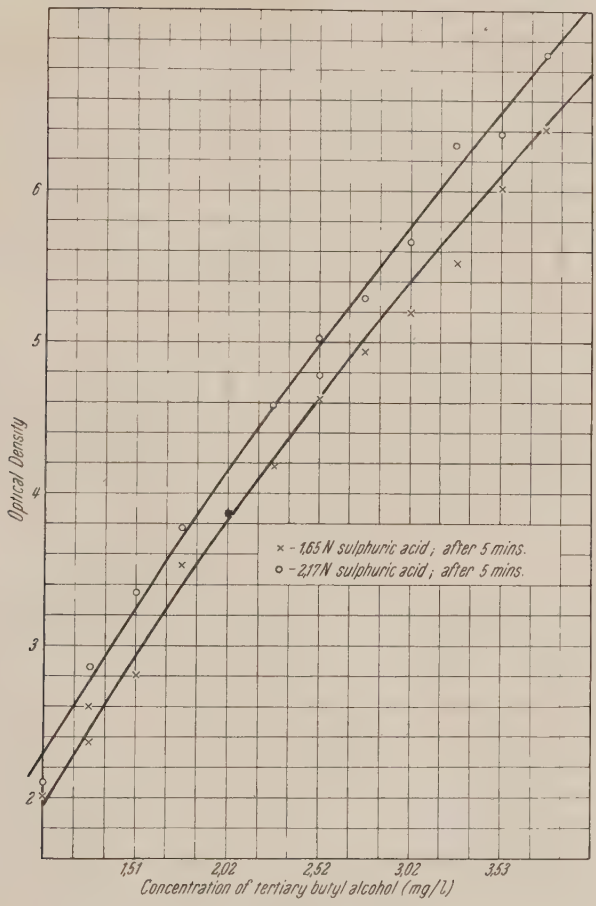

Fig. 2

are seldom more accurate than this, but in most methods the turbidity develops from the initial moment of mixing the reagents, so that error is introduced by difficultly controllable factors like speed of mixing. In the present method, turbidity develops later, on heating, and greater accuracy might be expected. It is essentially a preliminary study and improved accuracy might be achieved by careful attention to the following points;

1. optical similarity of the test-tubes used; this was in fact checked but precision apparatus could perhaps yield slightly more accurate values;

2. similarity of heat-conducting properties of the tubes. It was found that the solution in the tubes attained the bath temperature after about 1.5 minutes from the moment of placing in the bath. This was not checked in detail for the individual tubes and, clearly, a more rapid or slower temperature rise could influence the turbidity development;

3. mixing of the solution during this temperature rise, e. g., magnetically;

4. use of a colloid stabiliser like gum ghatti. The conditions aimed at obtaining the reading where the rate of turbidity decay was low, but at higher acid, mercury and alcohol concentrations, as seen in Table III, this was slightly higher.

A more accurate study of temperature and time factors would be possible by constructing a combined spectrophotometer/thermostat system. This would eliminate the intermittent removal of the tubes from the bath, with ensuing cooling-off.

It is hoped in later work to examine some of the points 1. to 4. mentioned above; and to study the chemistry of the method, including the influence of light on the mercury complex formed. It is also hoped to test further tertiary (and other) alcohols and perhaps some olefines, and to examine the influence of the presence of other organic compounds.

Summary

A rapid turbidimetric method for the analysis of very dilute aqueous solutions of tertiary butyl alcohol has been developed, using a mercuric sulphate/sulphuric acid reagent similar to the Denigès reagent. Concentrations as low as 1–6 mg/litre can be determined to within about 5% error.

Zusammenfassung

Eine schnelle turbidimetrische Methode zur Bestimmung sehr verdünnter, wäßriger Lösungen von tertiärem Butylalkohol wurde beschrieben. Sie beruht auf der Reaktion mit einer dem Reagens von *Denigès* ähnlichen Quecksilber(II)-sulfat-Schwefelsäure-Lösung. Konzentrationen von 1 bis 6 mg/l können mit einer Genauigkeit von etwa 5% bestimmt werden.

Résumé

L'auteur a mis au point une méthode turbidimétrique rapide pour l'analyse de solutions aqueuses très diluées d'alcool butylique tertiaire; à cette fin il emploie un réactif acide sulfurique-sulfate mercurique semblable à celui de *Denigès*. Dans ces conditions il est possible de déterminer des concentrations s'abaissant à 1—6 mg/litre avec une erreur inférieure à environ 5%.

References

[1] *G. Denigès*, C. r. acad. sci., Paris **126**, 1043, 1145, 1868 (1898).
[2] *J. Chatt*, Chem. Rev. **48**, 14 (1951).
[3] *A. Lindenberg*, C. r. soc. biol. Paris **125**, 135 (1937).

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A New Spot Test for Gold

By

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The test is based upon the formation of an orange-yellow chelate of gold(III) with phenyl-α-pyridyl ketoxime[1]. This chelate of gold is very stable and is extracted by chloroform from aqueous solutions of p_H 3 to 9.

Reagent Solution. A 1% solution of phenyl-α-pyridyl ketoxime in 95% ethanol was used as reagent.

Standard Gold Solution. Standard gold solution was prepared from gold(III) chloride and standardized according to *Beamish*[2]. Dilute solutions were prepared from this stock solution.

Performance of Test. One drop of weakly acidic or neutral solution is placed into the depression of a white spot plate and treated with one drop of reagent solution. If the test solution is strongly acidic, a few drops of 0.5 *M* Na_2CO_3 are added to the mixture after the addition of the reagent solution. A yellow color indicates gold(III).

Interfering Ions. Large amounts of alkali metals, ammonium, alkaline earths, Ag(I), Tl(I), Pb(II), Cd(II), La(III), Al(III), Mn(II), Bi(III), Fe(III) as well as nitrate, sulfate, phosphate, borate, and acetate do not interfere and neither do moderate amounts of chloride and bromide. Platinum metal ions other than Pd(II) interfere because of their color. Cu(II), Ni(II), Co(II), and Pd(II) give colored chelates which prevent observation of the gold test. Most of these interferences may be circumvented, but palladium(II), Hg(II), cyanide, large amounts of bromide, iodide, and organic anions like oxalate, tartrate, and citrate render the gold test useless.

Sensitivity. In aqueous solution: limit of identification = 1 μg; dilution limit = 1 : 1000000.

In chloroform: limit of identification $= 0.5\,\mu g$; dilution limit $=$ 1 : 1000000.

After extraction from aqueous solution containing EDTA: limit of identification $= 2.5\,\mu g$; dilution limit $= 1 : 1000000$.

Detection of Gold in Presence of Platinum Metals. One drop of the weakly acidic or neutral test solution containing gold(III) and platinum metal ions excepting Pd(II) is taken into a 5-ml beaker and treated with one drop of the reagent solution and 10 drops of water. To the mixture is then added 0.5 to 1 ml of chloroform. The phases are intimately mixed with an extraction pipet[3] and eventually allowed to separate in the pipet. The chloroform is drained into the depression of a white spot plate. The presence of gold is shown by the yellow color of the chloroform extract. If the test solution is too acidic, a few drops of 0.5 *M* Na_2CO_3 solution is added to the mixture after the addition of the reagent.

Detection of Gold in Presence of Copper(II), Nickel(II), and Cobalt(II). A drop of weakly acidic or neutral test solution is treated in a 5-ml beaker with 10 drops of 0.1 *M* EDTA solution, one drop of reagent solution, and 0.5 to 1 ml of chloroform. The phases are well mixed by means of an extraction pipet[3] and allowed to separate in the pipet. The chloroform layer is drained into the depression of a white spot plate, where the yellow color of the gold chelate is observed. Unless the test solution is very strongly acidic, EDTA solution usually adjusts the p_H. Otherwise, the acid is neutralized by the addition of a few drops of 0.5 *M* Na_2CO_3 solution after the addition of the reagent. In presence of EDTA the test is less sensitive.

Acknowledgement

The author wishes to thank Professor *Philip W. West* for permission to use his laboratory facilities. The partial financial assistance by the Division of Research Grants, Public Health Service, is being gratefully acknowledged.

Summary

A new spot test for gold is based upon the formation of an orange-yellow chelate with phenyl-α-pyridyl ketoxime. Limit of identification: $0.5\,\mu g$ Au.

Zusammenfassung

Eine neue Tüpfelprobe für Gold beruht auf der Bildung einer orangegelben Innerkomplexverbindung mit Phenyl-α-pyridylketoxim. Die Erfassungsgrenze beträgt $0{,}5\,\mu g$ Au.

Résumé

Description d'un nouvel essai à la touche de l'or fondé sur la formation d'un chélate jaune-orangé par réaction sur la phényl-α-pyridyl cétoxime. La limite inférieure d'identification est 0,5 μg Au.

Bibliography

[1] *B. Sen*, Chem. and Ind. **1958**, 562.

[2] *F. E. Beamish, J. J. Russell*, and *J. Seath*, Ind. Eng. Chem., Analyt. Ed. **9**, 174 (1937).

[3] *J. K. Carlton*, Analyt. Chemistry **22**, 1072 (1950).

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The Microanalysis of Silicate and Carbonate Minerals

I. Determination of Ferrous Iron

By

J. P. Riley and **H. P. Williams**

With 1 Figure

(Received December 27, 1958)

A knowledge of the chemical compositions of the co-existing minerals in rocks is of great importance for understanding the chemical reactions occurring during diagenesis and metamorphism. Investigation of the compositions of such minerals has been greatly hindered by the difficulty of separating the 3-g to 5-g samples of the pure minerals, which are necessary for a complete analysis by the classical silicate analysis methods.

Quantitative spectrographic methods of analysis, while only requiring small samples, are generally not sufficiently exact for the study of small changes in the concentrations of the major components. Several workers[1–5] have described partial or complete schemes for the micro- or semimicro-determination of the major components of silicate rocks. In general, these methods are scaled down versions of the classical procedures, in which, after separation, the elements are determined gravimetrically or volumetrically. It seems to be commonly agreed[6,7] that micro-analysis of silicates demands a high degree of competence in the analyst, and that its inaccuracy and tediousness are such that it should only be attempted if the size of sample makes it essential. On the other hand, very satisfactory results can be obtained using semi-micro methods, with total samples of ca. 0.5–1 g. Much time is saved, compared with micro-analysis, by the shorter periods required for evaporation and filtration.

In order to reduce the time required for the analysis of silicates *Hedin*[8] has used spectrophotometric methods for the determination of eight of the major components of rocks. *Shapiro* and *Brannock*[9,10] have published schemes for the analysis of rocks using spectrophoto-

metric, flame photometric and chelatometric procedures. These methods have been studied statistically by *Mercy*[11]. *Corey* and *Jackson*[12] have described a semi-micro scheme employing similar methods, for the determination of the commoner components of silicate rocks, with the exception of H_2O, CO_2, FeO, MnO and P_2O_5, using a total sample of 0.2 g.

Chirnside[7] has very justifiably criticised these rapid procedures, because in several cases separations are carried out using a single precipitation, and there is a high probability that considerable amounts of the element to be determined will be co-precipitated; with less justification he has asserted that these methods are not rapid. In an attempt to obviate the necessity for using separations involving the risk of co-precipitation, the senior author[13] has described a scheme for the determination of nine of the major constituents of silicate rocks, in which either specific methods of determination are used, or separations are carried out by liquid-liquid extraction or ion exchange prior to determination.

This is the first of a series of papers describing methods for the micro-determination of the 13 major constituents normally determined in silicate and carbonate minerals. A total sample of ca. 0.05 g is necessary, and is used as shown in Table I. The accuracy of the methods is similar to the corresponding methods of classical silicate analysis.

Table I. Sample weights used for determinations

Oxide determined	Weight used (mg)
SiO_2	5
TiO_2, Fe_2O_3[0], Al_2O_3, MgO, CaO, MnO, Na_2O, K_2O, P_2O_5.	25
H_2O, CO_2	10
FeO	5
Total...	45

Owing to the difficulty of ensuring that small samples of materials as heterogeneous as many rocks are representative, it is recommended that the use of the micro-methods should generally be restricted to the analysis of minerals. If it is essential to analyse minute amounts of rocks or other heterogeneous material, it is advisable to grind the sample to pass a 140-mesh sieve: only in this way can a sample representative of the whole be taken for each determination. There is some risk of oxidation of ferrous iron during the grinding process, but this will not be serious if the grinding is not prolonged.

Determination of Ferrous Iron in Rocks

In the normal macro-method for the determination of ferrous iron in rocks the sample is decomposed in a closed platinum crucible by

boiling with a mixture of hydrofluoric and sulphuric acids. The hot mixture is poured into boric acid solution to complex the fluoride ions and the ferrous iron is determined by titration with standard dichromate or ceric sulphate solution. *Vincent* and *Phillips*[14] have used a scaled down version of this method to determine ferrous oxide in 15-mg to 20-mg samples of magnetite, averaging ca. 42% FeO. It is generally agreed that the principal source of error in these methods is aerial oxidation of the ferrous iron during the decomposition process, or to a lesser extent, during the titration. In order to minimise the risk of oxidation *Wilson*[15] opens up the sample in the cold with hydrofluoric acid in the presence of a known (excess) amount of ammonium vanadate; the amount of unreduced vanadate remaining is determined by titration with standard ferrous solution.

On the micro-scale, using samples of 3–5 mg, with average contents of ferrous oxide of less than 10%, the problem of preventing aerial oxidation of ferrous iron becomes paramount. Experiments were therefore made in which known amounts of ferrous ammonium sulphate in 50% sulphuric acid were heated for varying periods at 100° in stoppered polytetrafluoroethylene (Teflon) tubes. After cooling, the tubes were opened and their contents were rinsed into dipyridyl solution. Sufficient sodium acetate was added to bring the solution to p_H 5.0 to ensure complete formation of the red ferrous-dipyridyl complex. The solutions were diluted to 100 ml and their optical densities were measured at 522 nm to determine the ferrous iron remaining. It was found that no oxidation of ferrous iron occurred even after 2 hours if the Teflon tube was completely filled with the acid.

Since the majority of silicate rocks are not attacked by heating with sulphuric acid, it is necessary to use a mixture of hydrofluoric and sulphuric acids for their decomposition. The presence of much fluoride causes a serious reduction of the intensity of the colour of the ferrous-dipyridyl complex, presumably owing to the formation of a complex ferrous fluoride. No interference was experienced with a fluoride concentration of 40 mg/100 ml in the final solution; but greater concentrations than this could not be tolerated.

When ferrous ammonium sulphate was heated with a mixture of 1 part of hydrofluoric acid and 4 parts of 50% sulphuric acid in a Teflon tube as described above, only 70–80% of the ferrous iron was detectable with dipyridyl after 60 minutes heating. On the other hand, if a 1 : 9 mixture of hydrofluoric and 50% sulphuric acids was used, 97%, 96% and 93% recoveries of ferrous iron were obtained after heating for 20, 40 and 60 minutes respectively. The decrease in the recovery of ferrous iron on heating with hydrofluoric acid appears to be due to the slow formation of a stable complex fluoride.

A small amount of oxidation of the ferrous iron also occurs during the heating process, owing to the presence of dissolved oxygen in the acid mixture. It was found that more consistent results could be obtained using an acid mixture which had been freed from oxygen by blowing a current of nitrogen through it.

Using the 1 : 9 hydrofluoric-sulphuric acid mixture the decomposition of most silicate rocks and minerals is complete after less than 20 minutes. In order to ensure that the opening up process was complete a heating period of 40 minutes was used in all subsequent work.

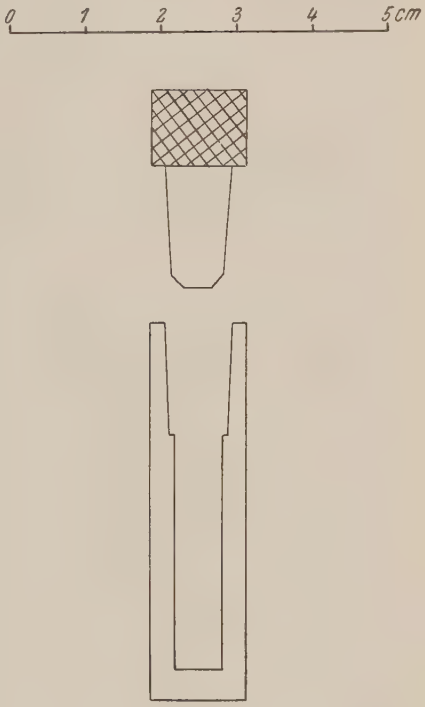

Fig. 1. Polytetrafluoroethylene tube for determination of FeO in minerals and rocks

Method

All measurements of optical density were made with a Unicam S. P. 500 spectrophotometer using 1-cm cells: the compensator cell contained distilled water.

Reagents

1. Hydrofluoric acid, 40% A. R.
2. Sulphuric acid, 50% *v/v*.
3. Acid mixture. Mix 10 ml of hydrofluoric acid with 90 ml of 50% sulphuric acid in a polyethylene bottle. Before use, pass a slow current of nitrogen through the liquid for 15 minutes using a polyethylene tube. Repeat the flushing with nitrogen for 5 minutes each day.
4. Acetone (10%). Dilute 5 ml of acetone to 50 ml with distilled water.
5. Dipyridyl solution. Dissolve 0.2 g of 2,2′-dipyridyl in 100 ml of 0.2 *N* hydrochloric acid.
6. Sodium acetate 2 *M*. Dissolve 136 g of sodium acetate trihydrate in water and dilute to 500 ml.
7. Ferrous ammonium sulphate A. R. Determine the ferrous iron content by titration with standard potassium dichromate.

Apparatus

The digestion tubes used for the decomposition of the samples are shown diagrammatically in Fig. 1. They are machined from 1.27-cm

diameter polytetrafluoroethylene (Teflon) rod. The body, which is 5 cm long, with an internal diameter of 0.635 cm, has a capacity of approximately 1 ml. It is tapered at the top (total angle of taper 10°) and is closed with a closely fitting tapered Teflon stopper. Several of the stoppered digestion tubes are held in a circular brass rack and their stoppers are clamped down with screws which are individually adjustable.

Before use, fill the tubes with a 1 : 1 mixture of concentrated nitric and sulphuric acids and allow to stand overnight. Rinse thoroughly, and dry at 110°. Occasionally, with certain types of sample, a deposit of siliceous material is formed inside the tubes: this is readily removed with 40% hydrofluoric acid or by passing a 0.635-cm twist drill down the barrel.

After repeated use the stoppers tend to become loose, due to enlargement of the socket of the body. Low results may then be obtained owing to the ingress of air. This difficulty may be overcome by turning ca. 0.4–1 mm off the top of the body.

Determination of Ferrous Iron in Rocks and Minerals

Grind the sample to pass through an 80-mesh sieve, and dry it at 110°. Weigh out into a Teflon tube, using a micro-balance, 3–5 mg of the dried sample. Add a few drops of the nitrogen-saturated acid mixture, using a polyethylene pipette. Shake the tube vigorously until the sample is suspended in the liquid. Some minerals, such as magnetite, are not wetted by the acid mixture and tend to cake in the tube; in such cases add 1 drop of 10% acetone and mix well before adding the acid mixture. Fill the tube with the acid mixture to just above the bottom of the taper and fit the stopper so that no air is trapped inside. Place the tube in the rack and clamp down its stopper. Mix the contents of the tubes by shaking well. Hang the rack freely in a bath of boiling water, so that the tubes are immersed for about half their length, and gently shaken by the movement of the boiling water.

After heating for 40 minutes remove the rack from the water bath, and immerse it to the same depth in cold water. After about 5 minutes, remove the tube from the rack, and wipe it dry with filter paper. Open it carefully, and transfer its contents to a 100-ml beaker containing 5 ml of dipyridyl solution. Rinse the stopper and the inside of the tube with a jet of water and add the washings to the beaker. Without delay add 20 ml of 2 *M* sodium acetate solution to bring the solution to approximately p_H 5. Again wash the tube with water and add the washings to the beaker. Test the tube for freedom from ferrous iron by addition of a few drops of dipyridyl and sodium acetate solutions. If the rock or mineral has been completely digested the liquid will be free from solid matter. Quantitatively transfer the contents of the beaker to a

100-ml graduated flask and dilute to volume. If the sample contains more than 20% of FeO the solution should be diluted to 250 ml. Measure the optical density of the solution at 522 nm in a 1-cm cell.

Determine the reagent blank in the same manner but omitting the sample. Calibrate the method using weighed samples of ferrous ammonium sulphate equivalent to about 0.02, 0.05, 0.1, 0.2, 0.4, 0.6 and 0.8 mg of FeO instead of the mineral or rock sample. Beer's law is obeyed up to at least 0.8 mg FeO. An optical density of ca. 0.575 is obtained with 0.5 mg FeO.

Calibration Curve

Various weights of ferrous iron in the form of ferrous ammonium sulphate (purity 99.9%) were treated as described in the experimental section. The results (Table II) show that a high degree of consistency is attained and that Beer's law is obeyed up to at least 0.7 mg of FeO.

Interferences

Dipyridyl is practically a specific reagent for the determination of ferrous iron. Of the commoner elements only cuprous copper forms a coloured derivative with this reagent: Cuprous copper does not occur in silicate or carbonate minerals, and there is therefore no risk of interference from the cations normally present in silicate rocks. No interference is caused by up to 60% of ferric iron in the sample.

The presence of sulphide minerals in rocks is a possible source of error in both the macro and micro determinations of ferrous iron, since they may cause reduction of ferric iron to the ferrous form. This interference was investigated using 5-mg samples of several sulphide minerals

Table II. Calibration of method with ferrous ammonium sulphate

Weight of Ferrous ammonium sulphate (mg)	Equivalent weight of FeO (mg)	Optical density *	Optical density increment/mg FeO
0.087	0.016	0.017	0.1063
0.360	0.066	0.075	0.1136
0.764	0.140	0.160	0.1143
1.337	0.245	0.280	0.1143
1.998	0.366	0.423	0.1156
2.031	0.372	0.429	0.1153
2.533	0.468	0.540	0.1154
2.740	0.502	0.580	0.1155
2.947	0.540	0.625	0.1157
3.030	0.555	0.641	0.1155
3.548	0.650	0.752	0.1157
3.794	0.695	0.804	0.1157

* Less reagent blank.

(ground to pass a 140-mesh sieve). These samples, both alone, and in the presence of 1 mg of ferric iron, were heated with the acid mixture as described in the experimental section. There was, as would be expected, a considerable difference in the ease of attack of the acid mixture. Cinnabar, molybdenite and pyrite were only slightly attacked and caused slight reduction of ferric iron (less than 1%). Blende, on the other hand, was almost completely decomposed and yielded an amount of ferrous iron roughly equivalent to its sulphide content. The sulphide minerals in rocks may be more finely divided, and therefore more easily attacked than the samples used in this study; these results must, therefore, be only regarded as an indication that the presence of much sulphide in the sample may lead to results for ferrous iron which are too high.

Analysis of Rocks and Minerals

In order to test the accuracy of the micro-method, replicate analyses were made of several minerals and rocks, with FeO contents ranging from 0.3–28%. Duplicate determinations of ferrous oxide were made on the samples using the macro-method described by *Washington*[16]. The results of both sets of determinations are shown in Table III. They

Table III. Determination of ferrous oxide in rock and mineral samples

Sample No.	Type	Origin	FeO % macro method	FeO % micro method	
				Determinations	Average
W 1*	Diabase	Westerly, Rhode Island	8.79	8.79, 8.83, 8.71, 8.68, 8.71	8.74
G 1*	Granite	Centerville, Virginia	0.93	0.94, 0.93, 0.92	0.93
1544	Hornblende biotite granite	Newry, Co. Down, N. Ireland	2.29	2.23, 2.24, 2.21, 2.20, 2.26	2.23
2798	Metadolerite	Dhambad, India	10.29	10.24, 10.29, 10.35	10.29
672	Biotite-andesine-sillimanite schist	Cashel, Co. Galway, N. Ireland	9.76	9.84, 9.92, 9.87	9.88
3507	Hornblende gneiss	Laxford, Scotland	7.68	7.69, 7.68, 7.59, 7.67	7.66
3	Clay	Corfe Castle, Dorset	0.31	0.37, 0.38, 0.38	0.38
	Chamosite	Unknown	20.10	20.3, 20.1, 20.2	20.20
13420	Magnetite	Taberg, Sweden	28.8	28.9, 28.9, 29.0	28.9

* U. S. Geological Survey standard samples[17].

indicate that there is a satisfactory agreement between the two methods. The values obtained for samples W 1 and G 1 by both the macro and micro methods were in excellent accordance with the average values of 8.7% and 0.99% respectively, which were found in these samples during a collaborative study of methods of silicate analysis[17]. The standard deviations found for samples W 1 and 1544 were 0.07 and 0.03% FeO respectively.

Acknowledgement

The authors wish to thank Mr. *R. H. Tennant* for making the Teflon tubes and their rack.

Summary

A method is described for the determination of ferrous iron in 3-mg to 5-mg samples of silicate and carbonate rocks and minerals. The sample is decomposed in a stoppered polytetrafluoroethylene tube by heating for 40 minutes at 100° with 18 *N* sulphuric acid containing 10% by volume of 40% hydrofluoric acid. After cooling, the solution is treated with 2,2′-dipyridyl and brought to p_H 5.0 by the addition of sodium acetate solution. Ferrous iron is estimated spectrophotometrically as the resultant red ferrous-dipyridyl complex. Ferric iron does not interfere. Results obtained for a range of rock and mineral samples (0.3–29% FeO) agree well with the values obtained by the conventional method. At a level of about 9% FeO a standard deviation of ± 0.07% FeO was found.

Zusammenfassung

Beschreibung eines Verfahrens zur Bestimmung von Eisen(II) in Einwaagen von 3 bis 5 mg silikat- bzw. carbonathältigen Gesteinen oder Mineralen. Die Probe wird in verschlossenen Teflonröhrchen mit einem Gemisch von 18-n Schwefelsäure mit 10 Vol.% 40%iger Flußsäure 40 Minuten bei 100° aufgeschlossen. Nach dem Abkühlen versetzt man die Lösung mit α,α′-Dipyridyl und bringt mit Natriumacetat auf p_H 5. Die rote Farbe der Komplexverbindung wird spektrophotometrisch gemessen. Eisen(III) stört nicht. Die für eine Reihe von Gesteinen und Mineralen erhaltenen Resultate (0,3 bis 29% FeO) stimmen gut mit den Ergebnissen der konventionellen Methode überein. Bei der Größenordnung von etwa 9% FeO wurde eine Abweichung von ± 0,07% FeO gefunden.

Résumé

Description d'une méthode pour le dosage du fer ferreux dans des échantillons de 3 à 5 mg de roches et de minéraux silicatés et carbonatés. L'échantillon est décomposé dans un tube bouché de polytétrafluoroéthylène pendant 40 minutes à la température de 100° en présence d'acide sulfurique 18 N contenant 10% en volume d'acide fluorhydrique à 40%. Après refroidissement la solution est traitée par le dipyridyl-2,2′ et amenée à p_H 5,0 par addition d'une solution d'acétate de sodium. Le fer ferreux est estimé par spectrophotométrie sous forme du complexe rouge dipyridyl-ferreux formé. Les

ions ferriques ne gênent pas. Les résultats obtenus pour toute une série d'échantillons de roches et de minéraux (0,3 à 29% FeO) concordent d'une façon satisfaisante avec les valeurs numériques obtenues par la méthode habituelle. Pour une teneur d'environ 9% FeO on a trouvé un écart type de $\pm$ 0,07% FeO.

Literature

[1] *F. Hecht* and *J. Donau*, Reine und angewandte Mikrochemie in Einzeldarstellungen, Bd. I. Anorganische Mikrogewichtsanalyse. Vienna: J. Springer. 1941.

[2] *W. A. Guthrie* and *C. C. Miller*, Min. Mag. London **23**, 405 (1933).

[3] *K. Schoklitsch*, Mikrochem. **20**, 247 (1936).

[4] *C. C. Miller* and *R. A. Chalmers*, Analyst **77**, 2 (1952); **78**, 25, 686 (1953).

[5] *R. A. Chalmers*, Analyst **78**, 32 (1953).

[6] *A. W. Groves*, Silicate Analysis, 2nd Ed. London: Geo. Allen and Unwin Ltd. 1951.

[7] *R. C. Chirnside*, Proc. 11th Chemists Conference, British Iron and Steel Research Association, 1957.

[8] *R. Hedin*, Svenska Forskninginst Cement Betong Vid. Kgl. Tek. Högskol. Stockholm. 1947.

[9] *L. Shapiro* and *W. W. Brannock*, Rapid Analysis of Silicate Rocks. U. S. Geol. Survey Circ. No. 165 (1952).

[10] *L. Shapiro* and *W. W. Brannock*, Rapid Analysis of Silicate Rocks. U. S. Geol. Survey Bull. No. 1036 C (1956).

[11] *E. L. P. Mercy*, Geochim. Cosmochim. Acta **9**, 161 (1956).

[12] *R. B. Corey* and *M. L. Jackson*, Analyt. Chemistry **25**, 624 (1953).

[13] *J. P. Riley*, Analyt. Chim. Acta **19**, 413 (1958).

[14] *E. A. Vincent* and *R. Phillips*, Geochim. Cosmochim. Acta **6**, 1 (1954).

[15] *A. D. Wilson*, Bull. Geol. Survey, Gt. Britain No. 9, 56 (1955).

[16] *H. S. Washington*, The Chemical Analysis of Rocks, 4th Ed. New York: Wiley. 1930.

[17] *H. W. Fairbairn*, *W. G. Schlecht*, *R. E. Stevens*, *W. H. Dennen* *L. H. Ahrens*, and *F. Chayes*, A co-operative investigation of precision and accuracy in Chemical, Spectrochemical and Modal Analysis of Silicate Rocks. U. S. Geol. Survey Bull. No. 980 (1951).

From the Oceanography Department, The University, Liverpool

The Microanalysis of Silicate and Carbonate Minerals

II. Determination of Water and Carbon Dioxide

By

J. P. Riley and **H. P. Williams**

With 1 Figure

(Received December 27, 1958)

In an earlier paper[1] one of the authors has described a rapid method for the determination of water and carbon dioxide in rocks. In this procedure the samples were heated at 1100–1200° in a current of nitrogen; the resultant water and carbon dioxide were absorbed and determined gravimetrically. The method showed a standard deviation of $\pm$ 0.04% with rocks containing ca. 5% of water, when a 0.5-g sample was used.

A comparative study was made of the precision of several commonly used methods for the determination of water in rocks, using the above procedure for referee purposes. It was found that in general the former methods gave results which were too low and of poor reproducibility.

This paper describes a micro-method for the simultaneous determination of water and carbon dioxide in rocks and minerals, using samples weighing about 10 mg. It has been developed from the author's macro-method, which has been substantially modified. The apparatus used (Fig. 1) is, in general, similar to that employed for the micro-determination of carbon and hydrogen in organic compounds, with the following differences:

1. Nitrogen, which has been freed from oxygen and organic impurities, is used for sweeping out the water and carbon dioxide.

2. The furnace, which is stationary, heats the combustion chamber to 1100° or 1200°, depending on the type of sample to be analysed.

3. The only packings in the combustion tube are a copper spiral and a plug of silver wool, which are heated to 700–800°. These fillings serve to remove oxides of nitrogen and sulphur, formed by the combination

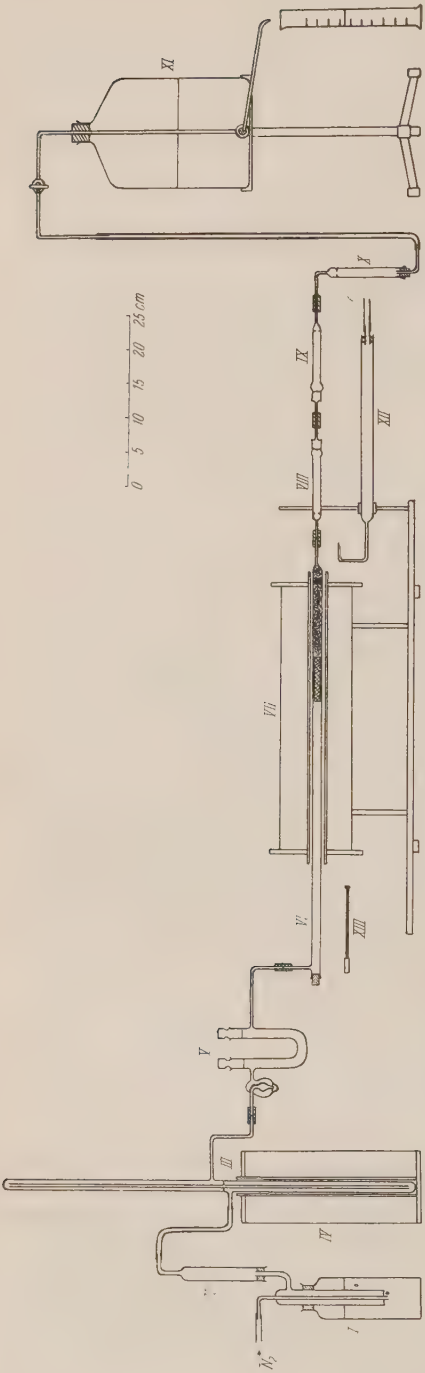

Fig. 1. Apparatus for the micro-determination of water and carbon dioxide in rocks and minerals *I* Pressure regulator, *II* Guard tube, *III* Preheater, *IV* Furnace for preheater, *V* Bubble counter and U-Tube *VI* Combustion tube, *VII* High temperature furnace, *VIII* Water absorption tube, *IX* Carbon dioxide absorption tube, *X* Guard tube, *XI* Mariotte bottle, *XII* Air purification tube, *XIII* Soft iron plunger

of traces of oxygen with the nitrogen gas, or with the sulphur of sulphide minerals present in the sample.

4. Phosphorus pentoxide has been used in addition to magnesium perchlorate for the absorption of water.

The sample, contained in a platinum boat, is pushed into the heating chamber at 1100–1200° by means of a soft iron plunger, using a magnet drawn along the outside of the tube. The liberated water and carbon dioxide are swept through the copper and silver packings, absorbed and determined gravimetrically.

Materials used for packings and connections

(a) Copper oxide, wire form, diameter 0.54 mm, length 2–4 mm, micro-analytical reagent grade.

(b) Copper, wire form. Heat the above copper oxide to a dull red heat and drop it into methyl alcohol. Dry at 130° before use.

(c) Platinised asbestos.

(d) Copper gauze, 40-mesh. Reduce with methanol as described above and dry at 130°.

(e) Silver wool, micro-analytical grade.

(f) Asbestos, micro-analytical reagent grade, ignited at 700°.

(g) Soda asbestos, micro-analytical reagent grade, 14–22-mesh.

(h) Phosphorus pentoxide–pumice mixture. Shake together approximately equal weights of phosphorus pentoxide and pumice stone (6–16-mesh). Store the mixture in a bottle with well fitting cork, which is protected with a piece of thin polyethylene sheeting.

(i) Magnesium perchlorate, microanalytical grade.

(j) Conditioned rubber tubing as used for organic micro-analysis.

(k) Impregnated rubber tubing as used for organic micro-analysis.

Apparatus

1. Pressure Regulator (I)

Nitrogen (not of oxygen-free quality) is supplied to the pressure regulator from a standard commercial cylinder fitted with a multi-stage reducing valve and needle valve. The regulator is of the normal type used in carbon-hydrogen micro-analysis, as specified in British Standards Specification No. 1428, Part A 1. It is filled with heavy white oil, an is connected via a guard tube (II), containing calcium chloride and magnesium perchlorate, to the preheater.

2. Preheater (III)

This device serves to remove organic impurities and oxygen from the nitrogen gas. It is constructed of Pyrex or, preferably, of resistance glass. The internal diameters of the external and internal tubes are 1.4 cm and 0.3 cm respectively. The lower part, which is 28 cm long, is maintained at 525° by means of an electric heater (IV). It is packed with platinised asbestos for 7 cm below the point of entry of the nitrogen, followed by 10-cm layers of short lengths of copper oxide wire and copper wire. The filling is held in place with a plug of ignited asbestos. After a few weeks of continual use the copper wire becomes oxidised; it must be reduced by passing a current of coal gas or hydrogen through the heated tube. About half of the copper metal is then oxidised back with a controlled current of air or oxygen, to give copper oxide, for the oxidation of organic impurities in the nitrogen. The upper part of the preheater serves to cool the nitrogen before it is passed into the bubble counter and absorption U-tube, to which it is attached with conditioned rubber tubing.

3. Bubble Counter and U-Tube (V)

The bubble counter is used to check the rate of passage of nitrogen into the combustion tube. It is fused to the stoppered U-tube which absorbs water and carbon dioxide formed in the preheater by combustion of organic impurities in the nitrogen. The bubble-counter contains

concentrated sulphuric acid, which covers the tip of the inlet tube (internal diameter ca. 1.0 mm) to a depth of 5 mm.

The U-tube has an internal diameter of 1.5 cm and is 11 cm high; it is closed at each end with B 19 stoppers, which are sealed in with Krönig's cement. It is packed at the end nearest to the bubble counter with a 2-cm layer of magnesium perchlorate, followed consecutively by a 7-cm layer of soda asbestos, a 4.5-cm layer of magnesium perchlorate and a 3.5-cm layer of phosphorus pentoxide-pumice mixture. Each layer of filling is held in place with plugs of glass wool.

4. Combustion Tube (VI)

The combustion tube is constructed of translucent silica. It has a total length of 62 cm and an internal diameter of 0.9 cm; it ends in a tube 2.5 cm long, with an internal diameter of 0.25 cm. The side-arm inlet for the purified nitrogen is fused on about 1.2 cm from its mouth; it has an internal diameter of 0.25 cm, and is attached to the side-arm of the U-tube with aged rubber tubing. The mouth of the combustion tube is closed with a well-fitting rubber bung.

The filling of the combustion tube consists of a mat of silver wool against the outlet tube, followed successively by a compact layer of asbestos 6 mm thick, a 10-cm layer of silver wool, and a tightly fitting spiral of copper gauze 10 cm long.

The combustion tube is heated by means of the high temperature furnace (VII) so that the silver and copper packings are at 750–800°. The unpacked part of the tube–the heating chamber–is at 1100–1200°, depending on the type of sample being analysed. In order to slow down devitrification of the tube at the high temperature used, it is essential that it is scrupulously clean both inside and out before it is put into the furnace. Although a certain amount of sagging and distortion takes place, the normal life of a transulucent tube is several months, even at 1200°. The transparent silica tubes used in micro-carbon-hydrogen analysis should not be used as they soon devitrify at this temperature.

5. High Temperature Furnace (VII)

The high-temperature furnace consists of an alumina tube 47 cm long and having an internal diameter of 2.5 cm. It is wound over the central 36 cm with 0.914-mm Kanthal Al resistance wire; 18 cm are wound with 6 turns per cm and the remaining 18 cm (which surrounds the packed part of the combustion tube) with 4 turns per cm. The resistance wire is bedded in aluminous cement and the space between it and the 10.5-cm diameter brass outer jacket is insulated with pure alumina. A Variac auto-transformer is used to regulate the furnace to the desired temperature.

6. Absorption Tubes (VIII) and (IX)

Standard organic micro-analysis absorption tubes, conforming with British Standards Specification No. 1428, Part A 1, are used for the absorption of water and carbon dioxide. Their fillings are held in place with glass wool plugs. The stoppers are sealed in with Krönig's cement.

The water absorption tube (VIII) contains a 4.5-cm layer of magnesium perchlorate, followed by a compact wad of glass wool and a 1.5-cm layer of phosphorus pentoxide mixture. The carbon dioxide absorption tube (IX) is packed with a 2.5-cm to 3-cm layer of magnesium perchlorate at the end remote from the stopper, followed by a thin plug of glass wool. The rest of the tube is filled with soda-asbestos to within 5 mm of the ground glass joint. In use, the absorption tubes are connected head to head; all connections to the absorption tubes are made with impregnated rubber tubing, lubricated with glycerine if necessary.

The precision of the method is largely limited by the difficulty of bringing the absorption tubes to constant weight. It has been found that satisfactory constancy can be obtained by the following procedure. Handle the tubes always by the capillaries, hold the tube with chamois leather, clean the insides of the capillaries with a small piece of cotton wool on a wire probe, and wipe them outside with chamois leather. Transfer the cleaned tubes to the rack of the wiping machine and wipe for 8 seconds each. Place the rack and tubes by the micro-balance. Determine the zero reading of the balance; 5 minutes after the conclusion of wiping place the water absorption tube on the stirrups of the balance and after 2–3 minutes weight it against its counterpoise. Replace this tube by the carbon dioxide absorption tube and weigh it against its counterpoise after 3 minutes.

7. Guard Tube (X)

The purpose of this tube, which is filled with magnesium perchlorate, is to absorb any moisture that may emanate from the Mariotte bottle.

8. Mariotte Bottle (XI)

The Mariotte bottle, which is of the conventional type (B. S. S. 1428, Part A 1), serves to measure the volume of nitrogen passing through the system during the determination; it also supplies sufficient suction to overcome the resistance of the absorption tubes to the passage of the gas.

9. Air-Purification Tube (XII)

To replace the nitrogen in the absorption tubes and to cool them quickly after absorption of water and carbon dioxide is complete, a

current of purified air is aspirated through them. The air is freed from water and carbon dioxide by passing it through the tube (XII), which is 24 cm long and has an internal diameter of 2 cm; the tube is packed with a 5-cm layer of magnesium perchlorate, followed successively by 5-cm layers of soda-asbestos, magnesium perchlorate, and phosphorus pentoxide-pumice mixture. When not in use both ends of the tube are kept stoppered with glass plugs.

10. Weighing Boats

The platinum boats weigh approximately 0.5 g and are 2.2 cm long over-all, 4 mm wide and 4 mm deep. If readily fusible minerals or rocks are analysed it is sometimes found that the sample has fused during the determination and adheres strongly to the boat. The fused mass can usually be removed by heating the boat to redness and quenching it in water; if this treatment fails the sample and boat should be fused with sodium carbonate in a platinum crucible at bright red heat.

11. Soft Iron Plunger (XIII)

The platinum boat containing the sample is pushed into the heating chamber of the combustion tube by means of a soft iron plunger, which is moved up and down the tube using a magnet applied externally. This plunger consists of a brass rod 12 cm long and 3.15 cm in diameter, which is screwed at either end into cylindrical soft iron heads. These heads have a diameter of 7.2 mm; the one which is used for pushing the boat is 5 mm long, the other, on which the magnet acts is 2 cm long. The plunger should only be handled with forceps and when not in use it should be kept in a well stoppered test-tube.

Determination of Water and Carbon Dioxide

Regulation of Nitrogen Flow

Pass a current of nitrogen through the pressure regulator so that about 2–3 bubbles per second are escaping to the atmosphere. Raise or lower the central glass unit of the regulator until about 1 bubble of gas per second passes through the bubble counter (V), when the constricted end of the combustion tube is open to the atmosphere. By means of the needle valve reduce the rate of escape of nitrogen to the air through the regulator to 1 bubble per second. With the furnace at 1100° flush out the apparatus with nitrogen for several hours before use, with the absorption tubes connected. If the apparatus is in continual use the nitrogen may be left flowing night and day.

Temperature of Furnace

For the analysis of the majority of mineral samples the heating chamber should be at 1100°. If the mineral to be analysed is known to be difficult to decompose, the temperature should be raised to 1200°.

Procedure

Suspend a platinum boat from a platinum wire hook and heat it to bright redness in a gas flame. Allow it to cool for a few minutes on the copper block of a micro-desiccator. Weigh out about 10 mg of the sample (dried at 110°) into the boat. Stopper the rubber tube at the narrow end of the combustion tube with a piece of glass rod with a fire polished end. Remove the bung from the other end, and insert the boat. Push the plunger into the tube behind the boat so that its larger head is opposite the sidearm. Replace the bung and remove the stopper from the narrow end of the tube. Flush the combustion tube with nitrogen for 10 minutes. While the apparatus is flushing weigh the absorption tubes, as described on p. 530. Connect the weighed absorption tubes head-to-head and make a glass-to-glass connection. Attach them to the combustion train so that the water absorption tube is connected glass-to-silica to the narrow end of the combustion tube; the free end of the carbon dioxide absorption tube is joined to the guard tube (X). With the tap of the Mariotte bottle closed, the flow of nitrogen through the bubble counter (V) should soon cease if the apparatus is free from leaks.

Open the tap on the Mariotte bottle (XI) and allow water to drip from the sidearm into a graduated cylinder. Adjust the angle of the sidearm so that the flow rate is 5–6 ml per minute. When the rate of flow is steady, push the plunger and sample as far as possible into the heating chamber using a strong magnet, withdraw the plunger to its original position immediately. Allow 130–150 ml of nitrogen to pass through the apparatus and then close the tap on the Mariotte bottle. Disconnect the end of the water absorption tube from the combustion tube and immediately connect it to the air purification tube. Stopper the end of the combustion tube. Open the tap on the Mariotte bottle and aspirate 30 ml of air through the absorption tubes. Disconnect the absorption tubes, clean their capillaries, wipe immediately and weigh them as described on p. 529.

Remove the bung from the combustion tube. Using a hooked 0.91-mm diameter Kanthal wire mounted in a glass rod, hook out the soft iron plunger and transfer it to its test-tube. Remove the platinum boat from the combustion chamber using the same hook. Insert the plunger and a boat containing the next sample, which has been weighed out while the absorption tubes were being swept out with air. Replace the

stopper and unplug the opposite end of the combustion tube. Allow the apparatus to flush with nitrogen while the absorption tubes from the previous determination are being weighed. Continue the determination, as described above, when the weighing has been completed.

At the beginning of each day's work, it is advisable to "condition" the apparatus by running an unweighed sample containing 3–5% of water as described above. The apparatus blanks should be determined each week by analysis of a sample of mineral having a known water and carbon dioxide content (i. e. determined by the macro method[1]). In a normal working day of 8 hours 7 or 8 determinations of water and carbon dioxide can be performed.

Determination of Water and Carbon Dioxide in Rocks and Minerals

In order to test the precision of the proposed method, replicate micro-analyses for water and carbon dioxide were made on a number of rocks (ground to pass a 120-mesh sieve). The results of the micro-method, which have been rounded off to the nearest 0.05% for water, and 0.1% for carbon dioxide, are shown in Table I, together with the values obtained for the same rocks for water by the macro-method[1], and for carbon dioxide chemically[2]. They show that there is good agreement for both water and carbon dioxide between the values obtained by the macro and micro-methods. The reproducibility of the latter is satisfactory;

Table I. Simultaneous determination of water and carbon dioxide in silicate rocks

Method	Water and carbon dioxide found in samples											
	2096 BL		672 BL		2122		2157		W 1		G 1	
	% H_2O	% CO_2	% H_2O	% CO_2	% H_2O	% CO_2	% H_2O	% CO_2	% H_2O	% CO_2	% H_2O	% CO_2
Macro-method	4.12	0.2	2.98	0.5	1.31	0.12	0.60	0.1	0.58	0.15	0.29	< 0.1
Micro-method	4.05	0.4	2.90	0.6	1.25	0.0	0.60	0.1	0.45	0.0	0.25	0.1
	4.05	0.3	2.85	0.5			0.70	0.2	0.60	0.2	0.20	0.2
	4.05	0.1	2.95	0.6			0.55	0.1	0.50	0.2	0.30	0.1
	4.10	0.1							0.45	0.1	0.30	
	4.10	0.3										
Mean....	4.07	0.2	2.90	0.6	1.25	0.0	0.62	0.1	0.50 ~ 0.1		0.27	0.1

Sample No. *Rock type.*

2096 BL Garnet-sillimanite-biotite schist.
672 BL Biotite-garnet schist.
2122 Granite.
2157 Biotite granite.
W 1 Diorite
G 1 Granite } U. S. Geological Survey standard rocks[3].

the standard deviations of the water and carbon dioxide figures, assessed from the analyses of sample 2096 BL are $\pm 0.05\%$ and $\pm 0.14\%$ respectively.

The samples W 1 and G 1 were those used in the collaborative study of the precision and accuracy of silicate analysis carried out by *Fairbairn* et al[3]. The average found by 6 analysts of the U. S. Geological Survey for the water contents of these rocks ($0.45 \pm 0.05\%$ and $0.31 \pm 0.08\%$ respectively) agree satisfactorily with the values found in the present study by both the macro and micro techniques.

Some minerals, such as staurolite and topaz, do not lose their water completely below 1100°, but it is lost rapidly at 1200°. The values found for three of these resistant silicates (ground to pass an 80-mesh sieve) by the micro-method, at a decomposition temperature of 1200°, are shown in Table II. Check determinations were also made as described by *Groves*[2] using sodium tungstate as flux, and by the author's macro-method[1]. The results obtained by all three methods show excellent agreement.

Table II. Determination of water in resistant silicates

Method	Water found in		
	Phlogopite %	Topaz %	Staurolite %
Macro-method[1]	2.77	1.66	1.87
Sodium tungstate flux[2]	2.72	1.69	1.83
Micro-method	2.80	1.80	1.90
	2.75	1.90	1.85
	2.70	1.80	1.85
	2.75	1.75	1.80
Mean	2.75	1.81	1.85

The micro-method was also used for the analysis of a number of carbonate minerals, rich in carbon dioxide. The results are shown in Table III, together with carbon dioxide contents found chemically[2] and in some cases also by the macro-combustion method[1]. In each case the concordance is good for both water and carbon dioxide.

The presence of organic matter or graphite in the sample gives rise to high results for the carbon dioxide content, since such materials are burnt at least partly, to carbon dioxide by traces of oxygen remaining in the nitrogen gas. The micro-method should, therefore, not be used for the determination of carbon dioxide in such samples.

Table III. Determination of water and carbon dioxide in carbonates

Method	Water and carbon dioxide found in									
	Calcium carbonate *		Oolitic limestone		Siderite		Magnesite		Dolomite	
	% H_2O	% CO_2	% H_2O	% CO_2	% H_2O	% CO_2	% H_2O	% CO_2	% H_2O	% CO_2
Macro[1]	0.0**	—	—	—	0.2	—	0.8	50.4	0.4	47.3
Chemical[2]	—	44.0**	—	42.6	—	38.7	—	50.2	—	47.3
Micro	0.1	43.8	0.6	43.3	0.2	38.9	1.0	50.5	0.4	47.5
	0.0	44.0	0.5	43.2	0.2	38.8	0.6	50.4	0.4	47.3
	0.1	44.0	0.5	42.9	0.2	39.0	0.8	50.3	0.4	47.6
			0.5	43.0						
Mean	0.1	43.9	0.5	43.1	0.2	38.9	0.8	50.4	0.4	47.5

* Analytical grade chemical dried at 300°.
** Theoretical values.

The interference of sulphide-sulphur in the determination of carbon dioxide was investigated by heating 0.7-mg samples of chalcopyrite (equivalent to 0.35 mg of sulphur) in the micro-apparatus. In no case was the gain in weight of the carbon dioxide absorption tube significant.

Acknowledgement

The authors wish to thank Mr. *R. H. Tennant* for constructing the high temperature furnace, and the furnace for the preheater.

Summary

A method is described for the simultaneous determination of water and carbon dioxide in 10-mg samples of rocks and minerals. The sample is heated at 1100–1200° in a current of purified nitrogen, and the resultant water and carbon dioxide are absorbed and determined gravimetrically. The method has been used for the analysis of both carbonates and silicates (including those which only lose their water above 1100°). The method showed a standard deviation of $\pm$ 0.05% H_2O for a sample having a water content of 4.1%, and of $\pm$ 0.24% CO_2 with a sample containing ca. 43% CO_2. About eight determinations can be made per day.

Zusammenfassung

Beschreibung eines Verfahrens zur gleichzeitigen Bestimmung von Wasser und Kohlendioxyd in 10-mg-Proben von Gesteinen und Mineralen. Die Probe wird in gereinigtem Stickstoff auf 1100 bis 1200° erhitzt, Wasser und Kohlendioxyd werden absorbiert und gravimetrisch bestimmt. Das Verfahren wurde zur Analyse von Carbonaten und Silikaten (einschließlich jenen, die ihr Wasser erst über 1100° abgeben) verwendet. Es zeigt eine

Standardabweichung von $\pm$ 0,05% H_2O bei Proben mit einem Wassergehalt von 4,1% und von $\pm$ 0,24% CO_2 bei Proben mit etwa 43% Kohlendioxyd. In einem Arbeitstag können etwa acht Bestimmungen durchgeführt werden.

Résumé

Description d'une méthode pour le dosage simultané de l'eau et de l'anhydride carbonique dans des échantillons de roches et de minéraux de 10 mg. L'échantillon est chauffé à la température de 1100—1200° dans un courant d'azote purifié; l'eau et l'anhydride carbonique qui se dégagent et sont entraînés, sont absorbés et dosés gravimétriquement. La méthode a été employée pour l'analyse des carbonates et des silicates (y compris ceux qui ne perdent leur eau qu'au-dessus de la température de 1100°). La précision de la méthode est caractérisée par un écart type de $\pm$ 0,05% H_2O pour un échantillon ayant une teneur en eau de 4,1% et de $\pm$ 0,24% CO_2 pour un échantillon contenant environ 43% d'anhydride carbonique. Il est possible d'effectuer environ 8 déterminations par jour.

Literature

[1] *J. P. Riley*, Analyst **83**, 42 (1958).

[2] *A. W. Groves*, Silicate Analysis, 2nd Ed. London: George Allen and Unwin Ltd. 1951.

[3] *H. W. Fairbairn*, A Co-operative investigation of precision and accuracy in chemical, spectrochemical and modal analysis of silicate rocks. U. S. Geol. Survey Bull. **580**, 21 (1951).

From the Laboratory of Prof. Dr. A. Sá, Universidad Nacional de Buenos Aires

Detection of Barium and Strontium in the Insoluble Sulfates*

By

P. Luis

With 1 Figure

(Received December 29, 1958)

Burford and *Caley*[1] reduce by heating with hydriodic acid. Similarly the sulfates are converted to perchlorates by evaporation with perchloric acid and potassium iodide, and an acetone extract of the residue is tested for barium and strontium. The efficiency of the rhodizonate test is improved by performing the test in a small area and by using an oxalate reagent for differentiating barium and strontium instead of the hydrochloric acid recommended by *Feigl*[2]. The latter reagent causes the fading of the coloration when only small quantities of barium are present, which are then mistaken for strontium; this failing has also been observed by *Charlot*[3].

Fig. 1. Glass Spoon

A chromate separation is used for the detection of small quantities of one metal in presence of large quantities of the other. *Feigl*'s[2] method of separating on spot test paper which has been impregnated with potassium chromate fails with small amounts of strontium.

A glass spoon (Fig. 1) of 0.2-, 1.0-, to 1.5-ml capacity has been used for evaporation over the flame and extraction.

Reagents

All reagents used were of analytical grade. Ammonium iodide may be taken in place of potassium iodide, but the latter was used, because

* Presented before the Congreso Ibero Americano de Microquímica, Lima, Perú, 1958.

it happened to have higher purity. In addition to acetic acid, acetone, iodide, and perchloric acid, the following are needed:

ammonium carbonate reagent, saturate 4 *M* ammonia with ammonium carbonate;

chromate reagent, dissolve 4 g CrO_3 in 20 to 30 ml water, add a solution of 12 g neutral ammonium acetate in 50 ml water, mix and dilute to 100 ml; if the solution of ammonium acetate is not neutral, treat it with ammonia or acetic acid and use bromothymol blue as an external indicator;

oxalate reagent, add 5 ml concentrated ammonia solution to 100 ml saturated solution of sodium oxalate;

sodium rhodizonate, prepare a saturated solution by dissolving less than one milligram of it in a few drops of water; prepare a fresh solution for each working period.

Procedure

In the glass spoon, Fig. 1, or in a micro crucible, treat about 0.5 mg of the insoluble sulfate, which must not contain lead, with 25 to 30 μl of 12.5% KI solution and about 75 μl 60% $HClO_4$. Heat the spoon evenly by performing a circular motion with it 2 or 3 cm above a microflame. Effervescence is soon followed by evolution of iodine vapors. When the white fumes of perchloric acid appear, gradually lower the spoon until it begins to touch the flame. Keep it in motion until the absence of fumes indicates that the acid has been completely expelled. Allow the spoon to cool, and then repeat the treatment with iodide and perchloric acid as described. This time make certain that the perchloric acid is completely removed to prevent its interference with the rhodizonate test.

Treat the cold residue with 70 μl acetone and tilt the spoon so that the whole residue becomes moistened. The perchlorates of the alkaline earths dissolve readily. Separate the extract from the insoluble potassium perchlorate by taking it up with a capillary pipet[4]. If too much of the acetone should have evaporated, treat the residue in the spoon with 50 μl more of it and take also this extract into the pipet. Reserve the residue in the spoon.

Preliminary Test. Place a small amount of rhodizonate solution on spot test paper to wet an area of 3- to 4-mm diameter. Holding the capillary pipet in horizontal position, touch its tip to the center of the reagent spot to deliver such a small amount of the acetone extract that it will not spread beyond the edge of the rhodizonate spot. Allow to dry, which will take only a few seconds.

A red spot indicates barium or strontium. If no coloration develops or the red coloration is light, add and evaporate additional portions of

the acetone extract as directed above until either an intense red spot is obtained or until one third of the whole extract has been added to the small area. About 0.002 μg barium or 0.01 μg strontium will give a light red spot. If a red spot is obtained, treat it with several small drops of oxalate reagent. Three things may happen:

(a) the red spot persists unchanged, which means that barium is present and some strontium may be present;

(b) the spot becomes colorless or brownish yellow, which proves that strontium is present, but does not exclude small amounts of barium;

(c) the red spot becomes lighter, but does not disappear; this proves that both barium and strontium are present, and their relative amounts may be estimated from the intensity of the spot before and after adding the oxalate reagent.

Final Test for the Minor Component. In the instances (a) and (b) continue testing as follows. Transfer the extract left in the capillary pipet to a centrifuge cone and repeat the extraction of the residue in the spoon with three more portions of 50 to 70 μl of acetone. Use the same capillary pipet for the transferring of the successive extracts to the centrifuge cone. Evaporate the collected extracts in the cone by blowing a stream of air on the surface of the liquid, and remove the last traces of solvent by heating on the steam bath.

Treat the residue in the cone with 50 to 70 μl of water and tap the cone so that the water will get to all residue left on the interior walls. Add 10 to 15 μl of chromate reagent and allow to stand for two to three minutes. Spin the cone in the centrifuge and then inspect the tip for the presence of a yellow precipitate. About 1 μg barium will give a precipitate in presence of 250 μg of strontium[6,7]. On the other hand, even 500 μg strontium will not give a precipitate under the conditions of the test.

For the detection of small amounts of strontium, transfer the yellow solution above the barium chromate precipitate to another centrifuge cone and treat it there with 20 to 25 μl ammonium carbonate reagent and about 50 μl acetone[5]. Allow to stand for a few minutes and then centrifuge. Since a white precipitate may be calcium carbonate, confirm the presence of strontium as follows. Remove and reject the centrifugate and wash the precipitate once with 50 μl of a mixture of equal volumes of acetone and water. Treat the washed precipitate with 50 μl 0.1 m acetic acid, stir, spin, and transfer the centrifugate to a microspoon. Add a few microliters of perchloric acid and evaporate to dryness over a microflame. Make certain that the excess of perchloric acid is completely expelled.

Extract the cold residue with 50 μl acetone. Take the solution into a capillary pipet and perform the rhodizonate test as described above.

If necessary, add two thirds of the extract in small portions to confine the test into an area of 3 to 4 mm diameter and then add a droplet of rhodizonate since the reagent tends to fade; finally add the remaining third of the extract. If a distinct red spot is not obtained (less than 1 Sr to 70 Ba), perform a blank test as follows. Transfer 50 μl 1% barium chloride solution, which does not contain strontium, into a centrifuge cone, add 20 μl chromate reagent, and continue as described for the test. The blank will give a light yellowish brown spot which is quite different from the orange pink hue obtained with very small amounts of strontium. In this manner, 1.25 μg strontium may be recognized in presence of 250 μg barium. The sensitivity of the test for strontium increases noticeably as the amount of barium present decreases. Coprecipitation of strontium with the barium chromate would explain this observation.

Application of the Procedure

To obtain test mixtures with known ratios of barium to strontium, measured volumes of solutions of the salts were transferred to a microspoon and there converted to sulfate by evaporation to dryness with an excess of dilute sulfuric acid. The procedure was then applied to the residual sulfate mixtures. Consistently satisfactory results were obtained in over two hundred trials.

Strontium was found in medicinal barium sulfate as well as in natural barite. Conversely, barium was discovered in commercial strontium sulfate.

The described treatment with perchloric acid and iodide gets into solution practically all strontium sulfate and more than 90% of barium sulfate. Lead interferes and must be absent or removed by one of the known methods: The practicability of an analytical group consisting of the sulfates of lead, barium, strontium, and calcium is being investigated.

Summary

Detection of 0.002 μg barium given as barium sulfate or 0.01 μg strontium given as strontium sulfate and identification of the two metals in mixtures of the sulfates with limiting proportions of 1 Ba : 250 Sr and 1 Sr : 200 Ba is accomplished by conversion to perchlorate, suitable modification of the rhodizonate test, and combining the latter with a simple separation procedure. Depending upon the ratio of the two alkali earth metals, the whole procedure requires from 7 to 30 minutes.

Zusammenfassung

Der Nachweis von 0,002 μg Barium oder 0.01 μg Strontium ist möglich, wenn Bariumsulfat oder Strontiumsulfat vorliegt. In Mischungen der beiden

Sulfate kann 1 Teil Barium in Gegenwart von 250 Teilen Strontium und 1 Teil Strontium neben 200 Teilen Barium aufgefunden werden. Dies wird durch Aufschluß mit Perchlorsäure und Jodid, Extraktion der Perchlorate mit Aceton, geeignete Abänderung der Tüpfelprobe mit Rhodizonat und, wenn nötig, Zuhilfenahme eines einfachen Trennungsverfahrens ermöglicht. Je nach dem Mengenverhältnis der beiden Erdalkalien werden 7 bis 30 Minuten zur Ausführung der Nachweise benötigt.

Résumé

Il est possible d'identifier 0,002 μg de baryum ou 0,01 μg de strontium présent sous forme de sulfate de baryum ou sulfate de strontium. Dans les mélanges des deux sulfates, il est possible de déterminer une partie de baryum en présence de 250 parties de strontium et 1 partie de strontium en présence de 200 parties de baryum. Cette détermination est effectuée après attaque par l'acide perchlorique et un iodure, extraction du perchlorate par l'acétone, modifications appropriées de l'essai à la touche par l'emploi de rhodizonate et si nécessaire mise en œuvre d'une technique simple de séparation. Suivant la teneur relative des deux alcalino-terreux, l'identification peut être effectuée en un temps compris entre 7 et 30 minutes.

Literature

[1] *E. R. Caley* and *G. Burford*, Ind. Eng. Chem., Analyt. Ed. **8**, 63 (1936).
[2] *F. Feigl*, Mikrochem. **2**, 188 (1924).
[3] *G. Charlot*, Teoria y Metodos nuevos de Química Analítica Cualitativa. Madrid: Aguilar. 1954. p. 197.
[4] *H. Malissa* and *A. A. Benedetti-Pichler*, Anorganische qualitative Mikroanalyse. Vienna: Springer-Verlag. 1958. p. 11.
[5] *P. E. Williams* and *H. T. Briscoe*, Chem. News **145**, 177 (1932).
[6] *Thérèse Dupuis* and *C. Duval*, Bull. soc. chim. France **16**, 567 (1949).
[7] *P. E. Wenger* and *R. Duckert*, Réactifs pour l'analyse minérale, deuxième rapport. Basle: Wepf & Cie. 1945; transl., Organic Reagents Used in Qualitative Analysis. New York: Elsevier. 1948.

From the Laboratory of Prof. Dr. A. Sá, Universidad Nacional de Buenos Aires

Detection of Sulfuric Acid in Insoluble Sulfates

By

P. Luis

With 1 Figure

(Received December 29, 1958)

In a preceding paper[1], the author has described the detection of barium and strontium in insoluble sulfates. For the analysis of insoluble residues, it is also desirable to have a simple, direct, and sensitive test for the presence of sulfate. It is proposed, to this end, to heat the insoluble residue in a capillary with phosphoric acid and to identify the sulfuric acid in the distillate by adding calcium chloride and observing the crystals of gypsum under the microscope.

Procedure

Draw a capillary of 1 to 1.5 mm outer diameter and 24 to 26 cm length at the center of a piece of soft glass tubing of 5 to 6 mm outer diameter and 15 to 17 cm length. Then cut as indicated in Fig. 1*a* to obtain two pieces of apparatus.

With a capillary pipet, deposit about 10 μl of 85% phosphoric acid in the center of the wide tubing. Transfer some of the sample to be tested to this droplet by picking it up with the end of a bent platinum wire or glass thread, which has been moistened with an invisible amount of the phosphoric acid. The material detaches itself from the end of the wire when the latter is inserted into the test drop, Fig. 1*b*. Seal the opening of the wide tubing and, in the same operation, attach to it a 6-cm length of the same kind of tubing which is to serve for a handle in operations to follow, Fig. 1*c*.

To prevent phosphoric acid from entering the capillary, start heating the test drop by applying a strong Bunsen flame between the drop and the constriction leading to the capillary while rotating the tubing around its axis. Finally apply heat to the whole of the wide tubing containing

the test drop. Continue until the phosphoric acid has been converted to a white film coating the interior of the wide tubing and a droplet of distillate has collected in the capillary. Then fuse and draw off the capillary from the wide tubing as indicated in Fig. 1 *e*.

For the identification of the sulfuric acid in the distillate[2], transfer to a microscope slide 3 to 5 μl of 0.25% solution of anhydrous calcium

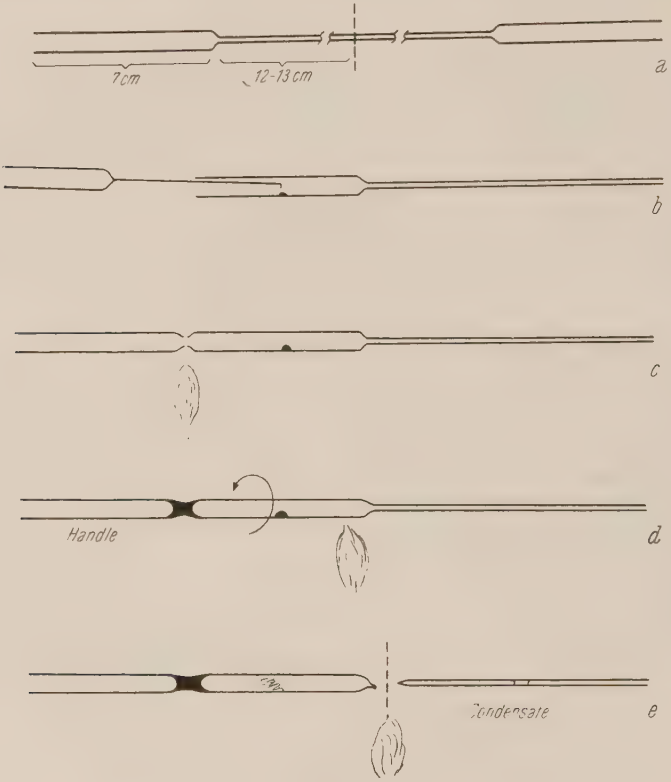

Fig. 1. Performance of Test

chloride, and evaporate the droplet to dryness. When the slide has acquired room temperature, treat the residue with the distillate from the capillary. Warm the microscope slide with a microflame, but make certain that the test drop does not evaporate. The presence of sulfate is indicated by the appearance of the characteristic needles and plates of $CaSO_4 \cdot 2\,H_2O$. If only very little sulfate is present, tiny needles will appear just before the drop dries up. It may be necessary to treat the dry residue of the test drop with 2 to 3 μl water, to warm it, and to start crystallization by scratching with a platinum wire or a glass needle

Application of Test

From numerous trials, it has been concluded that the procedure permits recognizing as little as 0.02 μg SO_4^{2-} given in the form of an insoluble sulfate. Interfering substances will usually be absent from an insoluble residue that has been extracted with acids. Inorganic and organic reducing agents might otherwise interfere by converting the sulfuric acid to sulfur dioxide, sulfur, or hydrogen sulfide. Water insoluble organic substances may be removed with the use of suitable solvents.

Summary

Heating of insoluble residue with phosphoric acid and testing the distillate with calcium chloride permits identifying 0.02 μg sulfate.

Zusammenfassung

Erhitzen des unlöslichen Rückstandes mit Phosphorsäure und Prüfen des Destillates mit Calciumchlorid erlaubt den Nachweis von 0,02 μg Sulfat.

Résumé

Il est possible d'identifier 0,02 μg de sulfate par chauffage du résidu insoluble en présence d'acide phosphorique et traitement du distillat par le chlorure de calcium.

Literature

[1] *P. Luis,* Mikrochim. Acta [Wien] **1959**, 536.

[2] *P. E. Wenger* and *R. Duckert,* Réactifs pour l'analyse minérale, deuxième rapport. Basle: Wepf & Cie. 1945; transl., Organic Reagents Used in Qualitative Analysis. New York: Elsevier. 1948. p. 215.

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Studies in Qualitative Inorganic Analysis. IX*

Detection of Aluminium Ion

By

W. F. Jones

(Received January 27, 1959)

Smith and *Shute*[1] have shown that when Aluminon (ammonium aurin-tricarboxylate) is used to detect aluminium after separation of the iron group in systematic qualitative analysis, positive results can be obtained when aluminium is absent. They found that small amounts of chromium(III) [formed by partial reduction of chromium(VI) with hydrogen peroxide after acidification] and iron(III) pass into the alkaline extract and give similar reactions to aluminium with the reagent. This was overcome by replacing hydrogen peroxide with bromine water for the oxidation of chromium(III), and masking the traces of iron(III) with Versene Fe-specific (N-N'-dihydroxyethylglycine).

The new procedure has been examined by *Waddams*[2] who found it efficient but somewhat lengthy. A more convenient alternative was therefore sought using a more selective reagent for aluminium.

Solochrome Cyanine, first proposed by *Eegriwe*[3], was examined. This reagent, which is less sensitive to iron(III) and chromium(III) than Aluminon, has now been in regular use by members of the Midlands Association for Qualitative Analysis for some time. The test is easily carried out, the reagent is sensitive even to very small amounts of aluminium ion, and is stable in aqueous solution.

Experimental

Preparation and Use of Reagent

A 0.1% aqueous solution is used; it is stored in a dark coloured bottle. The precipitate of aluminium hydroxide is dissolved in sodium hydroxide

* Part VIII. Mikrochim. Acta [Wien] **1958**, 571.

and a portion of this solution is added to the reagent in the presence of excess of ammonium acetate. If aluminium is present, the colour changes from orange-yellow to reddish purple.

The test must be carried out in weak acid solution since the colour of the reagent is purple in the presence of sodium hydroxide. The solution of the reagent in ammonium acetate must not therefore be added to the whole of the sodium aluminate extract.

The purple colour is also given by zirconium ion but the test is not affected in the ordinary course of phosphate separation using zirconium nitrate, since zirconium hydroxide is completely insoluble in sodium hydroxide.

Chromium(VI), when present in relatively large amount, imparts a red colour to the reagent, but this is easily distinguished from the colour given by the aluminium ion.

Recommended Procedure in Group Separation

Wash the iron group precipitate with water, add 3–4 drops 4 *N* NaOH and the same volume of water. Boil* and centrifuge.

Table I

<table>
<tr><th colspan="2">Residue</th><th>Solution</th></tr>
<tr><td colspan="2">Wash with water containing 1 drop 4 N NaOH. Add a few drops 4 N NaOH and an equal volume of 20 volumes H_2O_2. Boil 1 minute. Centrifuge</td><td rowspan="2">Add 2 drops to a mixture of 2 drops Solochrome Cyanine in 4 drops 50% ammonium acetate. A reddish purple colour or precipitate shows the presence of aluminium</td></tr>
<tr><td>Residue</td><td>Solution</td></tr>
<tr><td>Test for iron(III)</td><td>Test for chromium(VI)</td><td></td></tr>
</table>

Summary

The use of Solochrome Cyanine to test for aluminium ion in the iron group separation is recommended and is preferred to the use of Aluminon.

Zusammenfassung

Solochromcyanin wird für den Nachweis von Aluminiumionen bei der Trennung der Eisengruppe empfohlen, da es gegenüber Aluminon Vorteile bietet.

* An appreciable amount of chromium hydroxide dissolves in sodium hydroxide to form sodium chromite and the solution appears green in colour. In order to reprecipitate this as chromic hydroxide the solution must be boiled.

Résumé

L'auteur recommande l'emploi de solochrome cyanine pour rechercher l'ion aluminium après séparation du groupe du fer; il préfère ce réactif à l'aluminon.

References

[1] *S. B. Smith* and *J. M. Shute*, J. Chem. Education **32**, 380 (1955).
[2] *J. A. Waddams*, Private Communication.
[3] *E. Eegriwe*, Z. analyt. Chem. **76**, 438 (1929).

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Studies in Qualitative Inorganic Analysis. X*

The Separation and Identification of the Halides and Thiocyanate

By

R. Belcher and **W. I. Stephen**

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Many methods have been proposed for the detection of thiocyanate, chloride, bromide and iodide in admixture[1,2]. For some time we have used the method described by *Weisz*[3] and this has given excellent results in our own hands (when the method was first tested by us on 40 unknown combinations of these 4 ions, correct results were obtained in every case). Unfortunately, this method appears to demand too great an experimental ability particularly from the more inexperienced student and in certain of our teaching courses the results have been disappointing; hence a simpler and universally applicable method was sought.

The main problem is to ensure effective decomposition of the thiocyanate so that chloride can be detected finally with silver nitrate; the most promising method appeared to be that of *Hart* and *Meyrovitz*[2] who add lead nitrate to precipitate thiocyanate and destroy the residual amount left in solution by boiling with nitrite. Most of the iodide is also precipitated (lead iodide is more insoluble than lead thiocyanate) and traces left in solution are also destroyed by the action of nitrite. It is then only necessary to boil for a few seconds to destroy residual thiocyanate and iodide.

The tests are done as follows:

1. *Iodide:* The acidified test solution is spotted on filter paper and an *iodide-free* solution of starch is added; the paper is then spotted with sodium nitrite solution. A blue colour indicates *iodide.*

* Part IX. Mikrochim. Acta [Wien] **1959**, 544.

2. *Thiocyanate:* The main test solution is treated with a solution of lead nitrate and any precipitate is centrifuged off. (Yellow lead iodide precipitated at this stage confirms the presence of iodide.) A portion of the supernatant liquid is spotted on filter paper and is treated with 1% ferric alum solution. A red colour indicates *thiocyanate.* (There is insufficient iodide remaining in solution after treatment with lead nitrate to interfere with this test.)

3. *Bromide:* If thiocyanate or iodide is present, the main solution is treated with sodium nitrite solution and 4 *N* nitric acid; the solution is boiled until the evolution of nitrogen oxides is complete. (If thiocyanate is present, sulphate is formed during its decomposition and a precipitate of lead sulphate is obtained at the completion of the reaction.) The solution is allowed to cool and lead dioxide is added. On warming the mixture, bromine is evolved and is tested for using moist, fluorescein paper[4]. A red colour on the paper indicates *bromide.* (It is important that after the nitrite treatment, the solution be still acidic; more 4 *N* nitric acid should be added at this stage and if nitrite is still present, it should be destroyed completely.)

4. *Chloride:* If bromide is present, the solution is boiled gently for a short time to expel the remainder of the bromine. The solution is allowed to cool somewhat and the clear supernatant liquid is tested with silver nitrate solution. A white precipitate indicates *chloride.*

In the systematic anion scheme[5] the four ions are precipitated as silver salts and are released by reduction with zinc and acetic acid. The reduction occupies some 15 minutes, hence metathesis with ammonium sulphide was tried as an alternative[1]. This was found to be much more rapid; hence this method is now recommended.

Ferrocyanide, ferricyanide, sulphide, arsenite and periodate are also precipitated as the silver salts in the scheme. The first three anions are tested for on a portion of the precipitate and the other two anions are extracted with nitric acid from the remaining portion of the precipitate and are tested for separately. Since ferrocyanide and ferricyanide remain in the portion to be tested for thiocyanate, chloride, bromide and iodide it was necessary to examine their effect under the new conditions. It was found that there was no interference; ferricyanide is reduced by ammonium sulphide to ferrocyanide and the latter precipitates completely as lead ferrocyanide during the treatment with lead nitrate as described above. After the metathesis of the mixed silver salts with ammonium sulphide and ammonia, the precipitated silver sulphide is centrifuged off and the excess ammonia and ammonium sulphide removed from the solution by boiling. Before testing for iodide, the solution must be acidified with 4 *N* perchloric acid to avoid oxidation of ferrocyanide to ferricyanide by nitric acid. If ferricyanide is formed before the treatment

with lead nitrate, it escapes precipitation and subsequently interferes with the chloride test. It is unnecessary to centrifuge off the sulphur arising from the decomposition of the ammonium sulphide; most of it is removed during the precipitation with lead nitrate and any remaining as a suspension is removed during the subsequent treatment with nitrite.

Iodate and bromate are precipitated as silver salts in a later group in the systematic scheme. After reduction with sulphite, iodide and bromide ions were also liberated by reduction with zinc and acetic acid, but the ammonium sulphide treatment is now preferred for reasons given earlier. The complete revised scheme is described in full elsewhere[5].

Procedure

Tests for Halides and Thiocyanate (in presence or absence of ferro- and ferricyanide)

To the precipitate of silver salts which may contain AgCl, AgBr, AgI, AgCNS, $Ag_3[Fe(CN)_6]$ and $Ag_4[Fe(CN)_6]$ add 10 drops of concentrated ammonia solution and 3 drops of yellow ammonium sulphide. Break up the precipitate by stirring it with a glass rod and warm until the black silver sulphide coagulates. Centrifuge and reject the precipitate. Transfer the solution to a 5-ml beaker and boil to expel ammonia and to decompose the ammonium sulphide. When the solution becomes cloudy, add 5–6 drops of 4 *N* perchloric acid and continue heating until H_2S is completely removed.

(a) Spot 1 drop on filter paper; add 1 drop of *iodide-free* starch solution and spot with sodium nitrite solution.

Blue colour indicates Iodide.

(b) Add 5 drops of 1 *M* lead nitrate to the solution in the beaker and transfer the contents to a tube. Centrifuge. Transfer the solution to a clean beaker and spot 1 drop on filter paper. Add 1 drop of 1% ferric alum solution.

Red colour indicates Thiocyanate.

(c) If thiocyanate or iodide is present, add 3–4 drops of 20% sodium nitrite and boil until no more brown fumes are evolved (if thiocyanate and iodide are absent, proceed directly with the test for bromine). Remove the beaker from the heating block, allow to cool somewhat and add a further 2–3 drops of 4 *N* perchloric acid. Add a spatula-end of lead dioxide and quickly cover with a watch-glass with a strip of moistened fluorescein paper on the underside. Boil gently for a few seconds and rinse the paper under the tap.

Red colour indicates Bromide.

(d) If bromide is present, boil the uncovered contents of the beaker for 30 seconds to expel the remainder of the bromine. Allow to stand for 30 seconds and decant the solution into a tube. Centrifuge if necessary. Add silver nitrate solution.

White precipitate indicates Chloride.

Tests for Bromate and Iodate

Dissolve the washed silver halate precipitate in a few drops of 4 *M* ammonia solution, warm and add 3 drops of yellow ammonium sulphide. Boil for a few seconds to reduce the halates completely to halides; centrifuge off and reject the precipitated silver sulphide. Transfer the solution to the beaker and boil to expel ammonia and to decompose the ammonium sulphide. Proceed with the tests for bromide and iodide as described earlier.

Summary

A semi-micro procedure for the detection of chloride, bromide, iodide and thiocyanate is described. After metathesis of the silver salts with ammonium polysulphide and destruction of the excess sulphide, iodide is tested for with nitrite and starch, and if present, it is precipitated as lead iodide. Large amounts of thiocyanate are partly precipitated at this stage and the residual solution is tested with ferric alum for thiocyanate. This and traces of iodide are destroyed by boiling with nitrite. The solution is then treated with lead dioxide and the fluorescein test for bromide is applied. After boiling out the last traces of bromine, the solution is tested for chloride with silver nitrate.

Zusammenfassung

Ein Halbmikro-Verfahren zum Nachweis von Chlorid, Bromid, Jodid und Rhodanid wurde beschrieben. Nach Umsetzung der Silbersalze mit Ammoniumpolysulfid und Zerstörung des überschüssigen Sulfids wird mit Nitrit und Stärke auf Jodid geprüft, das dann gegebenenfalls als Bleijodid gefällt wird. Die Hauptmenge Rhodanid wird hierbei mitgefällt, das Filtrat wird mit Eisen(III)-alaun auf Rhodanid geprüft. Dieses und restliche Spuren Jodid werden durch Kochen mit Nitrit zerstört. Dann behandelt man die Lösung mit Bleidioxyd und prüft mit der Fluoreszeinprobe auf Bromid. Nach Verkochen der letzten Spuren Brom wird die Lösung mit Silbernitrat auf Chlorid untersucht.

Résumé

Description d'une semi-micro technique permettant de déceler les chlorures, les bromures, les iodures et les thiocyanates. Après double décomposition des sels d'argent en présence de polysulfure d'ammonium et après destruction de l'excès de sulfure, les iodures sont recherchés à l'aide de nitrite et d'emplois d'amidon; s'ils sont présents, ils sont précipités sous forme d'iodure de plomb.

Lors de cette opération, une grande proportion de thiocyanates précipite et l'on recherche dans la solution résiduelle ces thiocyanates à l'aide d'alun ferrique. Une ébullition en présence de nitrite permet de détruire ces thiocyanates ainsi que d'éventuelles traces d'iodures. La solution est alors traités par le bioxyde de plomb et les bromures sont recherchés par l'essai à la fluorescéine. Après avoir chassé les dernières traces de brome par ébullition, on recherche les chlorures dans la solution à l'aide de nitrate d'argent.

References

[1] *A. A. Noyes* and *E. H. Swift*, Qualitative Chemical Analysis of Inorganic Substances. New York: Macmillan. **1942**. p. 339.

[2] *D. Hart* and *R. Meyrovitz*, Ind. Eng. Chem., Analyt. Ed. **13**, 237 (1941).

[3] *H. Weisz*, Mikrochim. Acta [Wien] **1956**, 1226.

[4] *F. Feigl*, Spot Tests in Inorganic Analysis, 5th Edition. Amsterdam: Elsevier. 1958. p. 262.

[5] Midlands Association for Qualitative Analysis, "Semi-micro Qualitative Inorganic Analysis, Advanced Tables", 4th Edition. Birmingham. 1959. (Obtainable from Stanford and Mann Ltd., 72–73 New Street, Birmingham 2.)

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Studies in Qualitative Inorganic Analysis. XI*

The Oxidation of Hydrogen Sulphide to Sulphate by Nitrate Ions

By

R. Andrews, L. S. Bark, and W. M. Dowson

(Received January 27, 1959)

In the conventional scheme of qualitative analysis, hydrogen sulphide is passed into the weakly acid solution (about 0.3 *N*) to precipitate the copper/tin group sulphides; when arsenic(V) is present it must be reduced before passage of hydrogen sulphide. Alternatively, arsenic(V) sulphide can be precipitated by passing hydrogen sulphide into the solution made strongly acid with hydrochloric acid (to give a final concentration of about 6 *N* HCl). If there is any oxidation of hydrogen sulphide to sulphate, barium, strontium, and possibly calcium, will precipitate as insoluble sulphates with the copper/tin group sulphides.

It has been suggested that nitrate may oxidise hydrogen sulphide and should be removed before passing hydrogen sulphide, but probably the majority of workers make no attempt to follow this injunction and still obtain what are considered to be satisfactory results. Nevertheless, it is generally accepted that considerable losses of alkaline earths occur before they are normally separated (at the conventional Group V stage).

The work described in the present paper was undertaken to study the effect of nitrate on sulphate formation.

Experimental

Hydrogen sulphide was passed into solutions containing nitrate ions at low (0.3 *N*) and at high acidity (6 *N*). Sulphur was separated and after boiling out hydrogen sulphide the amount of sulphate formed

* Part X. Mikrochim. Acta [Wien] **1959**, 547.

was determined gravimetrically as barium sulphate. The influence of certain other ions was also investigated.

The results obtained indicate that the formation of sulphate at high acidity is dependent on the concentration of nitrate ions.

With 0.1 *M* nitrate not more than the equivalent of about 1 mg $BaSO_4$ per 1 ml of solution would be expected (experiments 1, 2 and 3).

Table I. Strongly Acid Solution. Final Concentration 6 *N* HCl
The temperature of the solution was maintained at 80° C whilst hydrogen sulphide was passed

Present		Volume used (ml)	Time hydrogen sulphide passed (mins)	$BaSO_4$ per 2 ml of solution (mg)	Remarks
1. NO_3^-	0.1 *M**	2	5	0.9	Sulphur extracted with $CHCl_3$; solution then evaporated to dryness
2. NO_3^-	0.1 *M**	20	5	2.9	Ditto
3. NO_3^-	0.1 *M**	10.5	5	Nil	Sulphur extracted with $CHCl_3$; solution not evaporated
4. NO_3^-	0.5 *M**	10.5	5	92.7 95.5 92.5	Ditto
5. Na_2HAsO_4	0.1 *M*	10.5	5	1. 0.4 2. Nil	Arsenic sulphides and sulphur separated by filtration
6. Na_2HAsO_4 $NaNO_3$	0.1 *M* 0.5 *M*	10.5	9	85.1 96.9 99.1	9 minutes required to precipitate arsenic sulphide completely. Precipitate removed by filtration
7. $FeCl_3$	0.1 *M*	10.5	5	Nil	Sulphur filtered off, reduction of the Fe^{3+} was incomplete
8. $FeCl_3$ $NaNO_3$	0.1 *M* 0.5 *M*	10.5	5	106.6 109.5	Sulphur filtered off, reduction of the Fe^{3+} incomplete. $BaSO_4$ precipitated from solution containing some Fe^{3+} and appeared slightly contaminated
9. $FeCl_3$ $NaNO_3$	0.1 *M* 0.5 *M*	2	1	51.7 53.6	Sulphur centrifuged off

* Nitrate was added as the sodium or potassium salt.

With higher concentrations of nitrate excessive amounts of sulphate are formed (experiment 4).

No sulphate is formed by iron(III) nor by arsenate at a concentration of 0.1 *M* (experiments 5 and 7).

The amount of sulphate formed by nitrate ions is not influenced by the presence of ferric ions nor by the presence of arsenate (experiments 6 and 8).

It would be expected, therefore, that if a solution contained barium ions and nitrate ions at a concentration of 0.1 *M*, at an acidity 6 *N* HCl, passage of hydrogen sulphide would not result in any significant loss of $BaSO_4$. This was confirmed experimentally (Table II).

Table II. Strongly Acid Solution. Final Concentration 6 *N* HCl

The temperature of the solution was maintained at 80° C whilst hydrogen sulphide was passed

Present	Volume used ml	Time hydrogen sulphide passed minutes	Barium determination as mg $BaSO_4$ per 2 ml original solution			
			Before hydrogen sulphide passed		After passage hydrogen sulphide and separation of precipitate	
			Theoretical	By determination	Formed during evaporation of solution	Remaining in solution
1. KNO_3 0.1 *M* $BaCl_2$ 0.035 *M*	20	5	16.2	15.4	1.2 (Sulphur extracted with $CHCl_3$)	12.7
2. KNO_3 0.1 *M* Na_2HAsO_4 0.1 *M* $BaCl_2$ 0.05 *M*	2	5	23.3	23.4		23.4

Table III. Weakly Acid Solution. Final Concentration about 0.3 *N* HCl

The temperature of the solution was maintained at 80° C whilst hydrogen sulphide was passed

Present	Volume used ml	Time hydrogen sulphide passed Minutes	$BaSC_4$ per 2 ml solution mg		Remarks
1. $NaNO_3$ 0.5 *M* $FeCl_3$ 0.1 *M*	2	1	3.6	3.9	Sulphur separated by centrifuge
2. $NaNO_3$ 0.5 *M* $FeCl_3$ 0.1 *M*	10	5	1.3	1.2	Sulphur separated by filtration

In 1. above, it would appear that a small amount of sulphate was formed by oxidation of a little colloidal sulphur during the evaporation of the solution. The barium remaining in solution after this treatment indicated a total loss of 2.7 mg $BaSO_4$/2 ml.

In 2. above, no loss of barium was shown during the precipitation of arsenic sulphide.

The amount of sulphate formed at low acidity, even with a very high concentration of nitrate, was very small indeed.

Table IV. Weakly Acid Solution. Concentration about 0.3 *N* HCl

Reduced by Boiling with Ammonium Iodide
To 2 ml of the weakly acid solution 5 or 10 drops of 20% NH_4I were added and after boiling for 1 minute, hydrogen sulphide was passed for 1 minute. The solution was reheated to boiling point and hydrogen sulphide passed for a further 1 minute. Any precipitate was centrifuged and sulphate was determined in the solution after boiling out hydrogen sulphide

	Present in solution before addition of NH_4I		$BaSO_4$ obtained mg
1.	$NaNO_3$	0.5 *M*	Nil
	$FeCl_3$	0.1 *M*	
2.	$NaNO_3$	0.1 *M*	Nil
	$FeCl_3$	0.05 *M*	
	Na_2HAsO_4	0.05 *M*	

The procedure given above reduces arsenate and separates arsenious sulphide quantitatively. The process does not result in formation of any significant amount of sulphate.

Conclusions

The formation of sulphate by oxidation of hydrogen sulphide with nitrate ions is significant only at high acidity and is then dependent on the concentration of nitrate.

It is necessary to pass hydrogen sulphide through a *strongly acid* solution in order to precipitate arsenic(V) sulphide from arsenate. Alternatively, arsenate can be reduced and hydrogen sulphide will then precipitate arsenic(III) sulphide from the weakly acid solution of arsenite.

In semi-micro qualitative analysis a sample weight of 10–25 mg is recommended; if as much as 7.5 mg nitrate ion were present, the concentration of nitrate in the solution before passage of hydrogen sulphide

(assuming acidity increased to about 6 *N* HCl, and final volume of solution 1.5 ml) would be rather less than 0.1 *M*. If barium were present, not more than the equivalent of 1 to 1.5 mg $BaSO_4$ would be expected to be lost.

If arsenic is not present and hydrogen sulphide is passed only through the weakly acid solution, very small or negligible amounts of sulphate are formed.

Alternatively, if arsenate is reduced by ammonium iodide and hydrogen sulphide passed through the weakly acid solution negligible amounts of sulphate would be formed.

Loss of alkaline earths must be due to other causes, e. g.

1. When destroying organic matter by oxidation with HNO_3; elementary sulphur is probably oxidised to sulphate.

2. Co-precipitation losses occur, probably when phosphate is separated, and in the iron group.

3. Carbonate impurities in the reagents may cause losses.

Summary

Two general methods are used to precipitate arsenic(V).

(a) As arsenic(V) sulphide by precipitation from hot solution at an acid concentration of 6 *N*.

(b) By prior reduction to arsenic(III) with ammonium iodide so that a low acidity can be maintained.

The effect of nitrate on the formation of sulphate from hydrogen sulphide has been studied at both acid concentrations.

When method (a) is used there is no fear of substantial sulphate formation provided that the nitrate concentration does not exceed 0.1 molar. This is not likely to occur when the specified amounts of sample used on the semi-micro scale are strictly adhered to.

Where method (b) is used there is no fear of significant sulphate formation even at abnormally high nitrate concentrations.

Provided that these conditions are followed there is no risk of significant loss of alkaline earths as sulphates, due to oxidation of hydrogen sulphide with nitrate. Such loss of alkaline earths which does occur, must be due therefore to other causes.

Zusammenfassung

Zur Fällung von Arsen(V) werden zwei verschiedene Methoden verwendet:

a) Fällung als Arsenpentasulfid aus heißer Lösung bei 6-n Säurekonzentration;

b) Fällung nach vorhergehender Reduktion mit Ammoniumjodid zu Arsen(III) bei niedriger Säurekonzentration.

Für beide Säurekonzentrationen wurde der Einfluß von Nitrat auf die Bildung von Sulfat aus Schwefelwasserstoff untersucht. Bei Fällung nach a)

besteht keine Gefahr, daß wesentliche Sulfatmengen gebildet werden, wenn die Nitratkonzentration nicht größer ist als 0,1-m. Das ist nicht wahrscheinlich, solange die Probemenge dem Halbmikromaßstab entspricht. Nach b) entstehen auch bei ungewöhnlich hoher Nitratkonzentration keine bedeutenden Mengen Sulfat. Werden diese Bedingungen eingehalten, so treten keine erkennbaren Verluste an Erdalkalien infolge Oxydation von Schwefelwasserstoff durch Nitrat auf, bzw. wenn sie auftreten, liegen andere Ursachen vor.

Résumé

On emploie deux méthodes générales pour précipiter l'arsenic(V).

a) Sous forme de sulfure d'arsenic(V) par précipitation d'une solution bouillante dont la concentration acide est 6 N.

b) Par réduction préalable en arsenic(III) à l'aide d'iodure d'ammonium de sorte qu'il soit possible de maintenir une faible acidité.

L'influence de la présence de nitrates sur la formation de sulfate à partir de l'hydrogène sulfuré, a été étudiée pour les deux concentrations d'acide.

Lorsqu'on emploie la méthode (a) une formation substantielle de sulfate n'est pas à craindre sous condition que la concentration de nitrate ne soit pas supérieure à 0,1 M. Il est d'ailleurs peu vraisemblable qu'il puisse en être ainsi lorsque l'ordre de grandeur des prises d'essais semi-microanalytiques est rigoureusement conforme à celui qui est spécifié dans le mode opératoire.

Lorsque l'on choisit la méthode (b) aucune formation sensible de sulfate n'est à craindre même dans le cas de concentrations de nitrates anormalement élevées.

Sous réserve que ces conditions soient respectées, il n'apparaît aucun risque de perte significative des alcalino-terreux sous forme de sulfates qui serait dûe à l'oxydation de l'hydrogène sulfuré par les nitrates. Si, en conséquence, on constate des pertes en alcalino-terreux elles doivent être attribuées à d'autres causes.

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Separation, Qualitative and Semi-Quantitative Determination of Micro-Amounts of Nickel and Cobalt by the Weisz Ring Oven Method

By

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A separation of nickel and cobalt is usually not necessary for the identification of these metals when they occur together, because the best qualitative reactions for these metals are dependable and sensitive also when there is an excess of the other metal. Often, however, in analysis of small samples which contain only micro-amounts of nickel and cobalt, it is necessary to separate these metals before the actual qualitative or quantitative determination. The aim of this investigation is to develop a micro-method for this separation and the subsequent determination, especially when one of the metals is in excess. The so-called Ring Oven method presented by *Weisz*[1] in 1954 appeared to offer good possibilities, because it had proved to be a dependable micro-method for separating some other metals from each other quantitatively[2]. Further, a general advantage of this method is that the analysis can be quickly performed using only one drop of the test solution and that it usually can be combined with a relatively accurate quantitative determination[3].

Method and Results

The Ring Oven method used in this investigation resembles paper chromatography in some respects. The method is based on the migration of the substances on the paper, but the R_f-values have not, however, in this case the same meaning as in chromatography. On the other hand, the separation is also based on the fact that the other components of the mixture can be fixed on the paper with suitable reagents. Through extraction with suitable solvents the soluble components can be set

into movement on the paper and they may be concentrated as sharp circular zones on the paper using the Ring Oven. Thus, using the right precipitating agents and solvents, mixtures of several components can be separated and the components can be identified with special reagents without interference from the other components. The colorimetric determination of the substances concentrated in the rings can often be performed more accurately and sensitively than by ordinary spot colorimetry.

Dimethylglyoxime[4] is well known as an excellent reagent for nickel, but cobalt, iron and palladium interfere in the reaction. By the aid of the Ring Oven method it seems, however, possible to eliminate the interference of cobalt and iron. This is also the most important as in practical work just these metals may be present when analysing nickel alloys. The occurence of palladium, on the other hand, is in such connections rare and consequently it is usually not necessary to take this into consideration. As dimethylglyoxime also can be used for the determination of cobalt[5], a method was developed in this investigation based on this reagent.

It was found through preliminary experiments that when using a filter paper saturated with dimethylglyoxime, nickel can be fixed by the Ring Oven in the middle of the paper, whereas the soluble dimethylglyoxime chelate with cobalt can be extracted with an ammonia solution and separated from nickel to a narrow ring which has the brown colour of the chelate. No special developing agent is therefore needed. When small quantities of nickel are in question it may be difficult to observe the nickel, after the extraction of cobalt, in the middle of the paper by the aid of the red colour of dimethylglyoxime. In that case it is, however, possible to concentrate nickel also on the Ring Oven to a much smaller area than that of the original spot in the middle of the paper. According to *Feigl*[6] nickel dimethylglyoxime forms a soluble bright red Ni^{IV}-chelate in the presence of oxidizing agents. This reaction was applied also in this investigation. It was found that the precipitated nickel dimethylglyoxime can be extracted to the periphery of the ring using as eluant an alcoholic solution of dimethylglyoxime containg bromine water as oxidant. In that way the sensitivity of the identification reaction for nickel is increased and the ring obtained may be used for quantitative determination following the principle of the Ring Oven method. If an extraction of nickel is to be performed from a sample containing cobalt, the latter must be extracted in the above-mentioned way to the periphery. After that the nickel dimethylglyoxime spot in the middle of the paper is cut out and placed on the Ring Oven in the middle of another filter paper. The nickel extraction can then be performed as described above.

If the sample contains iron, it must be noted that divalent iron forms a red dimethylglyoxime chelate[7] and consequently interferes with the separation. Divalent iron may, however, easily be oxidized but it should rather be removed because in the identification of cobalt large amounts of trivalent iron may interfere giving a similar colour to that of cobalt dimethylglyoxime. It is also possible to bind iron as a tartrate complex[7]. Further, when iron and cobalt are present at the same time, dimethylglyoxime may give a red colour although nickel is not present[8]. The formation of such a complex of iron and cobalt together on the filter paper must consequently be taken into account, although this, according to the experiments performed, seems to happen very rarely.

In this investigation mixtures of cobalt and nickel were analysed by the Ring Oven technique. It was found that quantitative separation can be performed even when there is a great excess of one of the components, no matter if this is cobalt or nickel. In such cases the determination of both metals with dimethylglyoxime is usually not possible without taking certain measures. Thus, a large amount of cobalt easily covers the colour due to a small amount of nickel. In the same way the colour of a small amount of cobalt cannot be seen beneath the colour of the nickel dimethylglyoxime. In such cases separation is necessary, so that the coloured cobalt and nickel chelates of dimethylglyoxime can be clearly distinguished from each other. In this investigation the sensitivity of the method was found to be 0.1 μg for nickel and 0.5 μg for cobalt. The method is best applicable as quantitative determination when the amount of nickel is in the range of 0.1–100 μg and that of cobalt 0.5–20 μg. For larger amounts it is difficult to compare the colour intensities of the rings, which is standard for the quantitative Ring Oven method[3]. However in the separation of small amounts of nickel from cobalt, for instance, the amount of cobalt can be considerably larger than 20 μg. In that case the amount of cobalt cannot be determined, but of nickel can, if it is within the given limits. In the same way it is possible to separate very small quantities of cobalt from large amounts of nickel. In that case, again, the quantity of nickel cannot be determined, but the cobalt can, if it is less than 20 μg. Thus, the method described appears to be applicable to the determination of micro-amounts of nickel in cobalt or the determination of micro-amounts of cobalt in nickel.

Experimental

When separating nickel and cobalt a Ring Oven constructed according to a model of *Weisz* was used, and further, Whatman No. 4 filter paper, which was soaked with a saturated solution of dimethylglyoxime in alcohol. The temperature of the Ring Oven was regulated by means of a Simmerstat Energy Regulator to slightly above 100° C. For the

extraction of cobalt an approximately 10 per cent aqueous solution of ammonia was used, added drop by drop in the middle of the paper. For the dissolving and extraction of nickel dimethylglyoxime to the periphery of the ring, a saturated dimethylglyoxime-alcohol solution was used to which $^1/_3$ by volume of bromine water had been added. After this the red colour of the Ni^{III}-dimethylglyoxime was developed by exposing the paper to ammonia vapours.

For the quantitative determination a standard series was prepared containing the following quantities of nickel and cobalt:

Nickel: 0.1, 0.2, 0.4, 0.8, 1.6 ... μg and

Cobalt: 0.5, 0.10, 0.20, 0.40, 0.80 ... μg.

For measuring the volumes a micro-pipette designed by *Ellilä*[9] was used. By the aid of this it is possible to measure extremely small volumes (10^{-4}–0.5 ml) with high accuracy.

Summary

A rapid and simple Ring Oven method is described for the separation and qualitative and semi-quantitative determination of nickel and cobalt. The method is best suited to small quantities, i. e., one drop of solution containing 0.1–100 μg nickel and 0.5–20 μg cobalt. It can also be applied to the micro-determination of nickel in cobalt or the micro-determination of cobalt in nickel.

Zusammenfassung

Eine schnelle und einfache Ringofen-Methode für die Trennung, den Nachweis und die halbquantitative Bestimmung von Nickel und Kobalt wurde beschrieben. Sie ist bestens geeignet für kleine Mengen, das heißt für einen Tropfen Lösung mit 0,1 bis 100 μg Nickel und 0,5 bis 20 μg Kobalt; sie kann auch zur Mikrobestimmung von Nickel in Kobalt oder von Kobalt in Nickel verwendet werden.

Résumé

Description d'une méthode au «four annulaire» simple et rapide pour la séparation et la détermination qualitative et semi-quantitative du nickel et du cobalt. La méthode est particulièrement appropriée aux dosages de faibles quantités, c'est-à-dire celles qui correspondent à une goutte de solution contenant 0,1—100 μg de nickel et 0,5—20 μg de cobalt. Elle peut être également appliquée au microdosage du nickel dans le cobalt ou du cobalt dans le nickel.

References

[1] *H. Weisz*, Mikrochim. Acta [Wien] **1954**, 140, 376; **1956**, 667; Chemical Age **1954**, 785; **1955**, 1319.

[2] *H. Weisz*, J. Chem. Education **32**, 70 (1955); *C. A. Bank* and *W. van der Eijk*, Chem. Weekbl. **51**, 351 (1955); *L. C. F. Blackman*, Mikrochim. Acta

[Wien] **1956**, 1366; *W. I. Stephen*, Mikrochim. Acta [Wien] **1956**, 1540; *P. J. Antikainen*, Suomen Kemistilehti B **31**, 277 (1958).

[3] *H. Weisz*, Mikrochim. Acta [Wien] **1954**, 460, 785; *W. Knodel* and *H. Weisz*, Mikrochim. Acta [Wien] **1957**, 417.

[4] *L. Tschugaeff*, Ber. dtsch. chem. Ges. **38**, 2520 (1905); *O. Brunck*, Z. angew. Chem. **20**, 1844 (1907); **27**, 315 (1914).

[5] *K. Kraut*, Z. angew. Chem. **19**, 1793 (1906).

[6] *F. Feigl*, Ber. dtsch. chem. Ges. **57**, 758 (1924); *A. P. Rollet*, C. r. acad. sci., Paris **183**, 212 (1926).

[7] *K. Heller* and *P. Krumholz*, Mikrochem. **7**, 218 (1929).

[8] *F. Feigl* and *H. J. Kapulitzas*, Mikrochem., Emich-Festschrift 128 (1930).

[9] *A. Ellilä*, Ann. Acad. Sci. Fennicae Ser. A II 51 (1953).

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Zur Kenntnis der anomalen Reaktionen bei der Aminostickstoff-Bestimmung. Die Reaktionen der NH—CO-Gruppierung mit salpetriger Säure

Von

Gerald Kainz und **Hans Huber**

Mit 7 Abbildungen

(Eingegangen am 9. Februar 1959)

Im Zuge der Aufklärung der Nebenreaktionen der van Slyke-Bestimmung haben wir die *Gaschromatographie* zur Untersuchung der gasförmigen Reaktionsprodukte eingesetzt. Diese Untersuchungen ermöglichten in Verbindung mit präparativen Befunden einen weitgehenden Einblick in das Reaktionsgeschehen bei der anomal reagierenden Gruppe der *Isonitrosoverbindungen*[1].

In der vorliegenden Arbeit haben wir uns die Aufgabe gestellt, das Verhalten von *Lactamen, die mit salpetriger Säure eine unbeständige Nitrosoverbindung bilden*, zu untersuchen, da auch diese Verbindungsklasse bei der van Slyke-Bestimmung eine anomale Gasentwicklung gibt. Später haben wir die Untersuchungen auf die *fünf- und sechsgliedrigen Heterocyklen* mit Harnstoffgruppierung ausgedehnt; denn es zeigte sich, daß die Reaktion beider Verbindungsklassen auf die Reaktion der NH—CO-Gruppierung mit salpetriger Säure zurückzuführen ist.

Vor allem interessierte uns, auf welchem Wege die anomale Gasentwicklung zustande kommt. Weiters wollten wir klären, warum gewisse Verbindungen mit NH—CO-Gruppierung eine anomale Gasentwicklung geben, andere hingegen nicht. Zuerst sei die Reaktion von 2,5-Diketopiperazin mit salpetriger Säure besprochen.

2,5-Diketopiperazin

Abb. 1 zeigt die Temperaturabhängigkeit dieser Reaktion zwischen 20 und 80° C. Während bei 20° C noch keine nennenswerte Gasentwick-

lung zu beobachten ist, findet man bei 40° C bereits 0,18 Mol N_2 und 0,03 Mol N_2O. Bei 80° C erreicht die N_2-Menge 0,38 Mol, die N_2O-Menge 0,08 Mol. CO_2 war im untersuchten Bereich nicht feststellbar.

Zur Klärung dieser Gasentwicklung haben wir vor allem zwei Reaktionsmöglichkeiten in Betracht gezogen:

1. Diketopiperazin erleidet eine *Hydrolyse* zu Glycylglycin bzw. Glycin; letztere geben mit salpetriger Säure eine Gasentwicklung.

2. Durch Reaktion mit salpetriger Säure bildet sich eine *N-Nitrosoverbindung, die unbeständig ist* und unter N_2-Entwicklung zerfällt.

Wir prüften zunächst, inwieweit die *erste Reaktionsmöglichkeit* (Hydrolyse) zutrifft. Es kam uns eine Arbeit von *Jaitschenkow*[2] zugute, der fand, daß zur quantitativen Hydrolyse von Diketopiperazin bei $p_H = 0{,}5$ 20stündiges Erhitzen auf 100° C nötig ist. Bei unseren Versuchen betrug das p_H (nach der Nitritzugabe) etwa 5,5, die Erhitzungsdauer 10 Minuten; die Reaktionsbedingungen waren also wesentlich milder. Trotzdem entstanden 0,46 Mol Gas. Wenngleich auch bei unseren Versuchen salpetrige Säure anwesend war, die zur Verschiebung des Hydrolysegleichgewichts beiträgt, so ist es doch unwahrscheinlich, daß die Hydrolyse in größerem Umfang an der anomalen Reaktion von Diketopiperazin beteiligt ist.

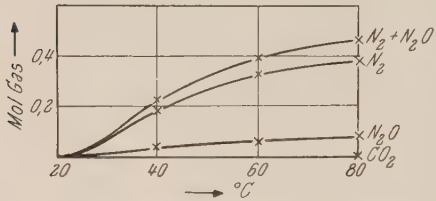
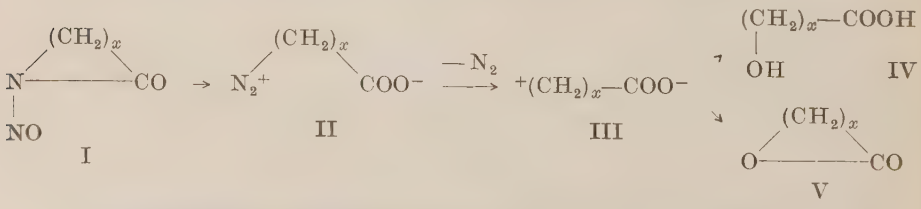


Abb. 1. Temperaturabhängigkeit der Reaktion von Diketopiperazin mit HNO_2

Wir prüften nun, inwieweit die *zweite Möglichkeit* (Bildung einer unbeständigen N-Nitrosoverbindung) zur Erklärung der anomalen Reaktion herangezogen werden kann. Es ist seit langem bekannt, daß viele Lactame mit salpetriger Säure eine N-Nitrosoverbindung bilden. *Bamberger*[3] fand nun, daß sich *N-Nitrosoverbindungen* mehr oder minder leicht *zu Diazoverbindungen isomerisieren können, die unbeständig sind und unter N_2-Entwicklung zerfallen.*

Huisgen[4] hat in eingehenden Untersuchungen den Reaktionsablauf bei verschiedenen Lactamen, wie ε-Caprolactam, Pyrrolidon, geklärt.



Demnach lagert sich das Nitrosolactam (I) in den isomeren Diazoester (II) um. Dieser spaltet N_2 ab, wodurch vorübergehend ein Carbeniumion (III)

auftritt. Dieses vereinigt sich entweder mit einem Anion, wie OH^-, zur Hydroxysäure (IV), oder geht durch intramolekularen Ringschluß in ein Lacton (V) über. Bei Caprolactam konnte das zu erwartende Lacton auch präparativ isoliert werden *(Nischk*[5]*)*.

Heyns und *Woyrsch*[6] haben die Dinitrosoverbindung von 2,5-Diketopiperazin dargestellt und zum isomeren Diazoester umgelagert. Dieser ist schon bei Zimmertemperatur unbeständig und spaltet sofort N_2 ab. Da die N_2-Entwicklung bei der Reaktion Diketopiperazin-HNO_2 auch unter unseren Bedingungen sehr leicht vonstatten geht, dürfte wohl das unbeständige N-Nitroso-diketopiperazin die Hauptursache für die anomale Gasentwicklung sein.

Parabansäure

Abb. 2 zeigt, daß man von Parabansäure ein ähnliches Diagramm wie von Diketopiperazin erhält. Bei 20° C werden 0,2 Mol N_2 entwickelt; durch Erhitzen auf 50° C läßt sich eine Steigerung auf 0,53 Mol erreichen. Die N_2-Bildung erfolgt demnach sehr leicht, während die N_2O- und CO_2-Entwicklung erst bei 50° C einsetzt und bei 80° C 0,17 Mol CO_2 bzw. 0,04 Mol N_2O erreicht.

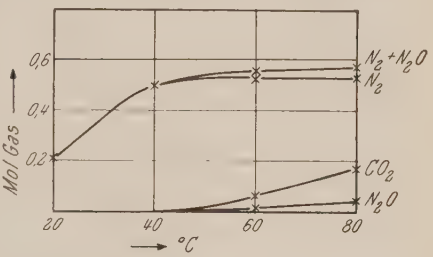


Abb. 2. Temperaturabhängigkeit der Reaktion Parabansäure—HNO_2 (30%ige Nitritlösung)

Es erhob sich nun die Frage, welche Reaktionsmöglichkeiten mit dem erhaltenen Diagramm am besten im Einklang stehen. Es war mit drei Möglichkeiten zu rechnen:

1. Die Parabansäure wird in Umkehrung der Bildungsreaktion *zu Oxalsäure und Harnstoff hydrolysiert*, wobei aus Harnstoff N_2 und CO_2 entstehen.

2. Die Parabansäure erleidet eine *partielle Hydrolyse zu Oxalursäure*, die anschließend desaminiert wird.

3. Die Parabansäure bildet eine *N-Nitrosoverbindung*, die sich zur isomeren Diazoverbindung umlagert und unter N_2-Entwicklung zerfällt.

Wir prüften zunächst die *erste Reaktionsmöglichkeit* (intermediäre Bildung von Harnstoff). Zutreffendenfalls mußte mit Harnstoff ein ähnliches Diagramm wie mit Parabansäure zu erhalten sein. Abb. 3 zeigt jedoch, daß sich Harnstoff grundsätzlich unterscheidet: die N_2-Menge verhält sich zur CO_2-Menge konstant wie 2 : 1. Dies trifft bei Parabansäure nicht zu. Somit scheidet diese Reaktionsmöglichkeit aus.

Die *zweite Reaktionsfolge* beinhaltet eine partielle Hydrolyse der Parabansäure zu Oxalursäure. Diese wird von salpetriger Säure unter Bildung eines Moles N_2 desaminiert. Die gebildete Carbamidsäure ist unbe-

ständig und gibt sofort 1 Mol CO_2 ab, wobei Oxalsäureamid entsteht. Dieses wird unter den Bedingungen der van Slyke-Bestimmung kaum angegriffen.

Somit sind bei dieser Reaktion gleiche N_2- und CO_2-Mengen zu erwarten. Da dies bei Parabansäure nicht zutrifft, so scheidet auch diese Reaktionsmöglichkeit aus.

Für die *dritte Reaktionsmöglichkeit* — Bildung einer unbeständigen N-Nitrosoverbindung — spricht, daß die Parabansäure mit salpetriger Säure leicht N_2 abspaltet und bei 50° C bereits das Maximum der N_2-Entwicklung erreicht ist. Da weiters die CO_2-Bildung erst ab 50° C einsetzt, muß man annehmen, daß aus Nitrosoparabansäure wie bei Nitrosocaprolactam eine cyklische Verbindung entsteht, die erst bei höherer Temperatur unter CO_2-Entwicklung gespalten wird.

Die Versuche mit Parabansäure zeigen, daß die Hydrolyse als primärer

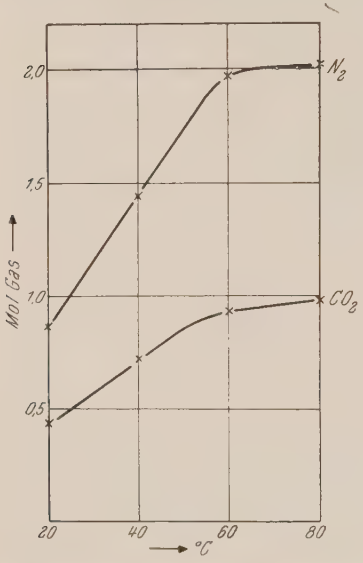


Abb. 3. Temperaturabhängigkeit der Reaktion Harnstoff—HNO_2 (30%ige Nitritlösung)

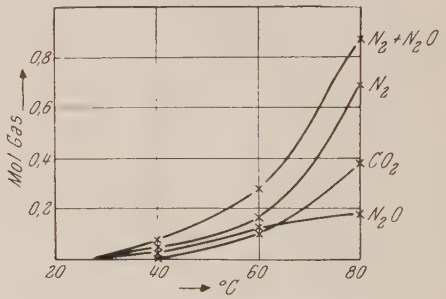


Abb. 4. Temperaturabhängigkeit der Reaktion Hydantoin—HO_2N

Reaktionsschritt kaum in Betracht kommt, daß hingegen ein Reaktionsablauf über eine Diazoverbindung sehr wahrscheinlich ist.

Hydantoin

Bei Betrachtung von Abb. 4 fällt zunächst der unterschiedliche Reaktionsverlauf gegenüber Diketopiperazin und Parabansäure auf. Demnach geht die Reaktion bei Hydantoin wesentlich schwieriger vor sich und ist, wie aus der Form der Reaktionskurve hervorgeht, bei 80° C noch nicht abgeschlossen. Bei 80° C werden 0,69 Mol N_2, 0,18 Mol N_2O und 0,38 Mol CO_2 entwickelt.

Wie bei obigen Verbindungen war zu entscheiden, ob vorwiegend eine Hydrolyse oder eine unbeständige N-Nitrosoverbindung der Anlaß zur Anomalie ist. Bezüglich einer möglichen hydrolytischen Spaltung

sei auf die Arbeiten von *Andreasch*[7] sowie *Ingold*[8] verwiesen, die feststellten, daß eine Hydrolyse in saurer Lösung äußerst schwierig ist. Es scheint demnach wahrscheinlich, daß die anomale Reaktion auch bei Hydantoin über eine N-Nitrosoverbindung verläuft, die sich teilweise zu einer Diazoverbindung umlagert. Bei deren Zerfall ist mit Stickstoff und, gemäß der oben angeführten Reaktionsfolge (I bis V), mit einer cyklischen Verbindung zu rechnen. Wir fanden bis 40° C nur N_2 (neben 0,02 Mol N_2O), was mit dieser Annahme in Übereinstimmung steht.

Bei der cyklischen Verbindung, die sich aus Parabansäure bildet, haben wir darauf hingewiesen, daß diese oberhalb 40 bis 50° C eine Ringsprengung erleidet, die zu einem weiteren Abbau führt. Beim Zerfall der cyklischen Verbindung, deren Entstehen aus Hydantoin anzunehmen ist, wären — bei quantitativem Verlauf — mit einem Mol

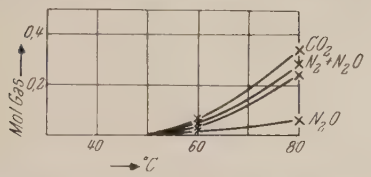


Abb. 5. Temperaturabhängigkeit der Reaktion Alloxan—HNO_2

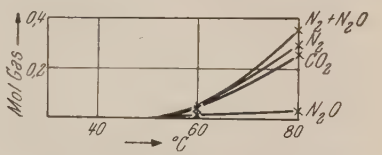


Abb. 6. Temperaturabhängigkeit der Reaktion Barbitursäure—HNO_2

CO_2 und einem Mol Glycin zu rechnen. Glycin würde sofort von HNO_2 desaminiert, so daß bei anomaler Reaktion 1,25 Mol N_2, 0,35 Mol N_2O und 0,6 Mol CO_2 zu erwarten sind (vgl. [9]). Tatsächlich fanden wir ab 40 bis 50° C einen sehr starken Anstieg der Gasmengen. Aus den gefundenen Daten läßt sich errechnen, daß etwa 0,30 bis 0,35 Mol Glycin entstehen.

Durch diese Sekundärreaktion erklärt sich der scheinbare Widerspruch, daß Hydantoin unter 40° C eine geringere anomale Gasentwicklung aufweist wie Parabansäure — daß also die anomale Reaktion erschwert ist —, während Hydantoin bei 80° C die Parabansäure stark übertrifft.

Alloxan

Wie aus Abb. 5 hervorgeht, setzt bei der Reaktion Alloxan—HNO_2 eine meßbare anomale Gasentwicklung erst ab 50° C ein und erreicht bei 80° C nur ein Drittel der Gasmenge aus Hydantoin. Als Erklärung nehmen wir auch bei Alloxan — in Analogie zu obigen Verbindungen — die Bildung einer unbeständigen N-Nitrosoverbindung an. Es sei jedoch betont, daß die anomale Reaktion bei Alloxan sehr erschwert ist. Dies steht in Übereinstimmung mit den Ergebnissen von *Huisgen*[4], wonach N-Nitrosolactame mit sechsgliedrigen Ringen nur sehr schwierig zu den unbeständigen Diazoverbindungen isomerisiert werden können. Demnach

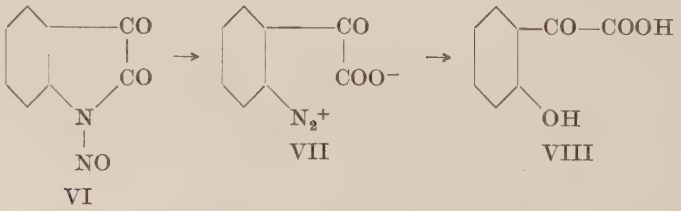
wurde auch nur ein Bruchteil der bei dieser Reaktionsfolge zu erwartenden Gasmengen (1 Mol N_2 und 1 bis 2 Mole CO_2 bei quantitativer Reaktion) gefunden.

Barbitursäure

Abb. 6 zeigt, daß diese Verbindung mit salpetriger Säure in ähnlichem Ausmaße wie Alloxan reagiert. Bei den Versuchen war eine Violettfärbung zu beobachten, die nach *Baeyer*[10] der dabei entstehenden Violursäure (= Isonitroso-barbitursäure) zuzuschreiben ist. Die aktive Methylengruppe der Barbitursäure ist also nitrosierbar. Die Beständigkeit der Violettfärbung bei 80° C sowie die nur geringfügige Erhöhung des $N_2 + N_2O$-Volumens gegenüber Alloxan läßt jedoch schließen, daß die Isonitrosoviolursäure nur in geringem Umfang mit salpetriger Säure weiterreagiert. Dies steht in Übereinstimmung mit unseren Beobachtungen[11] bei Malonester, der wohl nitrosiert wird, dessen Isonitrosogruppe aber auch weitgehend einem weiteren Angriff standhält. Bezüglich der Anomalie der beiden NH—CO-Gruppierungen gilt das bei Alloxan Gesagte.

Isatin

Das Ausmaß der Anomalie von Isatin ist, wie Abb. 7 zeigt, bedeutend größer als bei den bisher besprochenen Fällen. Neben einer eventuell in Frage kommenden Hydrolyse darf man auch hier zur Hauptsache eine N-Nitrosierung annehmen. *Huisgen*[4] beobachtete bei N-Nitrosooxindolen eine Isomerisierung zu Diazoestern, die sofort N_2 abspalten. Die Anwendung dieser Reaktionsfolge auf Isatin führt zu folgendem Schema:



VI VII VIII

Zunächst entsteht die N-Nitrosoverbindung (VI), die sich in den Diazoester (VII) umlagert. Da sich die Diazoniumgruppe am Benzolkern befindet, ist nicht mit einer spontanen N_2-Abspaltung zu rechnen. In weiterer Reaktionsfolge ist sodann die Ketosäure (VIII) zu erwarten.

Dies steht in Übereinstimmung mit unseren Versuchen (vgl. Abb. 7). Bei 20° C ist noch kein Stickstoff feststellbar. Hingegen zerfällt bereits die Ketosäure; die CO_2-Menge bei 20° C beträgt 0,4 Mol. Die Zunahme der Reaktionsgase mit steigender Temperatur ist sehr stark.

Bei 80° C geht sowohl die N_2- als auch die CO_2-Menge über die maximal zu erwartende Menge von einem Mol hinaus. Außerdem tritt ab 40° C

N_2O auf. Diese Befunde lassen darauf schließen, daß neben der Anomalie der NH—CO-Gruppierung noch *eine andere anomale Reaktionsfolge mitbeteiligt* ist. Nach obigem Schema wäre aus Verbindung (VIII) Hydroxybenzaldehyd zu erwarten. Wie wir[12] gefunden haben, weisen Phenole eine überaus starke anomale Gasentwicklung auf, wobei N_2, N_2O und CO_2 entstehen. Demnach tritt bei Isatin eine Überlagerung der Anomalie der NH—CO-Gruppierung mit einer Phenolanomalie auf.

Unsere Versuche über die anomale Gasentwicklung bei der Reaktion der NH—CO-Gruppierung mit salpetriger Säure haben also wahrscheinlich gemacht, daß eine hydrolytische Aufspaltung unter Bildung einer primären Aminogruppe nur in untergeordnetem Maße in Frage kommt. Als wahrscheinliche Ursache wird die Bildung einer N-Nitrosoverbindung angesehen, die sich mehr oder minder leicht zu einer Diazoverbindung umlagern kann. Diese ist unbeständig und zerfällt unter N_2-Entwicklung.

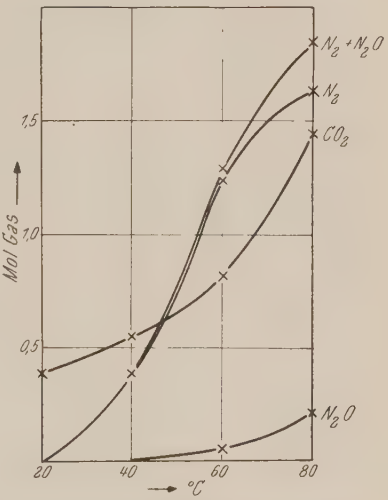


Abb. 7. Temperaturabhängigkeit der Reaktion Isatin—HNO_2

Bezüglich der Aminostickstoffbestimmung läßt sich aus diesen Ergebnissen ableiten, daß bei Vorliegen einer NH—CO-Gruppierung nur dann mit einer Anomalie zu rechnen ist, wenn beide Reaktionsstufen (1. N-Nitrosoverbindung und 2. Umlagerung zur Diazoverbindung) durchlaufen werden. Der erste Schritt kann bereits erschwert sein. So werden nach den Befunden von *Huisgen*[4] höhergliedrige Lactame schwer nitrosiert. Die anomale Reaktion bleibt dann aus. Aber auch der zweite Schritt kann erschwert sein. Zum Beispiel zeigen offenkettige aliphatische Verbindungen mit NH—CO-Gruppierung kaum eine Neigung zur Bildung eines Diazoesters. Auch in diesen Fällen bleibt die anomale Gasentwicklung aus. Es sind somit vor allem die fünf- und sechsgliedrigen Heterocyklen mit Lactamgruppe, bei denen *beide* Reaktionsschritte ablaufen und die dadurch die Anomalie geben.

Experimenteller Teil

Zur Aufnahme sämtlicher Diagramme wurde eine Aminostickstoffapparatur nach *Kainz*[13] benützt. Es wurden jeweils 8 bis 12 mg Substanz in das Reaktionskölbchen eingewogen und in 1 ml Eisessig + 1 ml 40%iger

Natriumacetatlösung gelöst oder suspendiert. Nachdem die Apparatur mit CO_2 (bei CO_2-Bestimmungen mit N_2) gespült worden war, wurden 2 ml 30%ige Natriumnitritlösung zugesetzt. Dann wurde 10 Minuten die angegebene Temperatur (20 bis 80° C) eingehalten und schließlich 20 Minuten bei 20° C nachgespült.

Bestimmung von Stickstoff und Distickstoffoxyd. An die Aminostickstoffapparatur wurde ein Gaschromatograph nach *Janak*[14] angeschlossen und das Reaktionsgas chromatographiert. Diese Anordnung wurde bereits in einer früheren Arbeit von uns[15] eingehend beschrieben.

Bestimmung von Kohlendioxyd. Die Reaktionsgase, die N_2, N_2O, CO_2 und NO enthielten, wurden durch den Bromat-Schwefelsäure-Wäscher der Aminostickstoffapparatur geleitet. Die bei der Oxydation der Stickoxyde entstehenden Bromdämpfe wurden mit gesättigter Natriumthiosulfatlösung, die 10% Dinatriumhydrogenphosphat und 10% Natriumdihydrogenphosphat enthielt, gewaschen. Die Reaktionsgase wurden mit Anhydrone getrocknet. Die Absorption von CO_2 erfolgte mit Natronasbest.

Zusammenfassung

Es wurde versucht zu klären, wie die NH—CO-Gruppierung mit salpetriger Säure reagiert, zumal diese Gruppierung bei der Aminostickstoffbestimmung Anlaß zu einer Anomalie gibt. Zunächst wurden die gasförmigen Produkte dieser bei verschiedenen Temperaturen durchgeführten Reaktion — N_2, N_2O und CO_2 — bestimmt. Daraus konnten wertvolle Hinweise über die in Frage kommenden Reaktionsmechanismen gewonnen werden. So ist eine hydrolytische Aufspaltung, die zu einer Verbindung mit primärer Aminogruppe führen würde, nur in sehr geringem Umfange zu erwarten. Sehr wahrscheinlich ist hingegen, daß zunächst eine N-Nitrosoverbindung entsteht, die sich in gewissen Fällen zur isomeren Diazoverbindung umlagern kann. Diese ist unbeständig und spaltet schon bei Zimmertemperatur Stickstoff ab. Zu dieser Umsetzung sind nur gewisse Verbindungen mit NH—CO-Gruppierung befähigt, und zwar vor allem die fünf- und sechsgliedrigen Heterocyklen mit Lactamgruppe; geradkettige aliphatische Verbindungen mit NH—CO-Gruppierung geben diese Reaktion nicht. Diese Deutung steht in Übereinstimmung mit den bisher empirisch festgestellten Befunden.

Summary

An attempt was made to discover how the NH—CO group reacts with nitrous acid, especially because this group leads to an anomaly in the determination of amino nitrogen. Firstly, the gaseous products of this reaction, conducted at various temperatures, were determined, namely N_2, N_2O, and CO_2. These data furnished valuable clues regarding the reaction mechanism being studied. For instance, a hydrolytic cleavage, leading to a compound with a primary amino group will occur to only a very minor extent. On the other hand, it is very probable that initially there will be production of a N-nitroso compound, which in some cases can rearrange into the isomeric diazo compound. The latter is unstable and breaks down, even at room temperature,

to yield nitrogen. Only certain compounds having the NH—CO group are capable of this reaction, and in fact the 5- and 6-membered heterocycles with a lactam group, especially; straight chain aliphatic compounds containing the NH—CO group do not give this reaction. This explanation is in agreement with the previous empirical findings.

Résumé

Les auteurs cherchent à élucider la réaction du groupement NH—CO sur l'acide nitreux, du fait que l'existence de ce groupement donne lieu à une anomalie lors de la détermination de l'azote aminé. Les produits gazeux N_2, N_2O et CO_2 qui se produisent à différentes température lorsqu'on effectue cette réaction ont été tout d'abord déterminés. Il en est résulté des indications précieuses sur le mécanisme de la réaction. C'est ainsi qu'une scission hydrolytique qui conduirait à une combinaison porteuse d'un groupement aminé primaire ne peut être attendue que dans une très faible mesure. Il est très vraisemblable, au contraire qu'il se forme tout d'abord une combinaison N-nitrosée qui dans certains cas peut se transposer en combinaison diazoïque isomére. Celle-ci est instable et se décompose dès la température ambiante en libérant de l'azote. Seuls certains groupements NH—CO sont susceptibles de subir cette décomposition, notamment les hétérocycles à 5 et 6 chaînons comportant un groupement lactame; les combinaisons aliphatiques à chaîne droite ne donnent pas cette réaction. Cette explication concorde avec les observations empiriques établies à ce jour.

Literatur

[1] *G. Kainz* und *H. Huber*, Mikrochim. Acta [Wien] **1959**, 337.
[2] *J. S. Jaitschenkow*, Biochem. Z. **190**, 114 (1927).
[3] *E. Bamberger*, Ber. dtsch. chem. Ges. **30**, 366 (1897); s. auch **27**, 914 (1894); **53**, 2513 (1920).
[4] *R. Huisgen*, Ann. Chem. **574**, 171 (1951); *R. Huisgen* und *J. Reinertsdorfer*, Ann. Chem. **575**, 197 (1951).
[5] *G. Nischk* und *E. Müller*, Ann. Chem. **576**, 232 (1952).
[6] *K. Heyns* und *O. F. Woyrsch*, Chem. Ber. **86**, 76 (1953).
[7] *R. Andreasch*, Mh. Chem. **23**, 810 (1902).
[8] *C. K. Ingold, S. Sako* und *J. F. Thorpe*, J. Chem. Soc. London **1922**, 1194.
[9] *R. Behrend* und *R. Niemeyer*, Ann. Chem. **365**, 39 (1924).
[10] *A. v. Baeyer*, Ann. Chem. **130**, 140 (1864).
[11] *G. Kainz* und *F. Kasler*, unveröffentlicht.
[12] *G. Kainz* und *H. Huber*, unveröffentlicht.
[13] *G. Kainz*, Mikrochim. Acta [Wien] **1953**, 349.
[14] *J. Janak*, Mikrochim. Acta [Wien] **1956**, 1038.
[15] *G. Kainz* und *H. Huber*, Mikrochim. Acta [Wien] **1959**, 51.

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Determination of Germanium After Extraction by Methyl Isobutyl Ketone. II

By

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With 2 Figures

(Received December 30, 1958)

Studies reported in a previous paper[1] showed that the extraction of germanium from hydrochloric acid solutions by methyl isobutyl ketone can be used as an efficient means of separating small amounts of the element, and that the reaction of the extracted germanium with molybdate, followed by reduction to a blue stable solution, can be performed directly in the ketone phase.

The possibility of using the organic solution as reacting medium seemed to deserve further study. For this reason the behavior of sensitive reagents in this particular medium was investigated.

Conditions were found that allow the use of the reaction of germanium with phenylfluorone directly in the organic phase, leading to very stable colored solutions. The reaction is instantaneous and twice as sensitive as the one carried out in aqueous solution with the same reagent. It thus enables rapid and reliable determination of minute amounts of germanium such as are found to occur in coals and other complex materials.

Apparatus, Solvent and Extraction Technique

A Beckman spectrophotometer, model DU, and 1 cm ground stoppered Corex cells were used throughout the study.

Commercial methyl isobutyl ketone (Shell) was purified as previously described[1] and distilled. It was freed from peroxide—when necessary—by shaking with ferrous sulfate, and thereafter redistilled. B. P. 111–113°.

The same extraction technique reported in the first publication[1] was employed.

Experimental

The effect of the variation of several factors on the reaction of germanium with phenylfluorone in organic medium was studied through a number of experiments carried out under different conditions, as given below.

In all these experiments solutions of germanium in methyl isobutyl ketone were obtained by extracting the element from 1.0 ml of acidified aqueous standard solution in the manner described in step 2 of the general procedure.

Effect of nature of solvent used in the preparation of the reagent solution. Solutions of phenylfluorone in pure methyl and ethyl alcohol, dioxane, ethylene glycol, acetone, methyl isobutyl ketone and ethyl acetate were tested as reagents for germanium dissolved in methyl isobutyl ketone. Another series of solutions was also prepared with the same water immiscible solvents pretreated with HCl or H_2SO_4 as well as with the miscible solvents to which a certain amount of both acids had been added. The solubility of phenylfluorone was found to increase considerably in the latter case. Results obtained in all experiments showed that solutions of phenylfluorone in acidic methyl and ethyl alcohols reacted more rapidily with germanium and produced a more intense color. Ethyl alcohol was thus chosen as solvent for the preparation of the reagent.

Effect of nature and concentration of acid used in the preparation of the reagent solution. All the solutions of phenylfluorone employed contained 0.02 g of the reagent, 5 ml of acid and enough ethyl alcohol to complete 100 ml.

In every case 3.0 ml of the reagent were added to the solution of germanium in methyl isobutyl ketone in a 10-ml volumetric flask, and the volume completed with ethyl alcohol.

Results are partly summarized in Table I and show that acid concentration is not critical provided sulfuric acid is used. Sulfuric acid was thus chosen for the preparation of the reagent solution employed in all subsequent experiments.

Table I. Effect of nature and concentration of the acid added to the reagent

Absorbance at 504 nm

Acid normality	1.0 μg Ge/ml			2.0 μg Ge/ml		
	HCl	H_2SO_4	$HClO_4$	HCl	H_2SO_4	$HClO_4$
2.6	0.254	0.256	0.255	0.492	0.498	0.498
5.2	0.240	0.255	0.254	0.497	0.498	0.492
10.4	0.191	0.255	0.209	0.371	0.495	0.414
12*	0.120	—	—	0.210	—	—

* According to *Schneider* and *Sandell*[2]: 16 ml of conc. HCl in 100 ml of reagent solution.

Effect of volume of the solution of germanium in methyl isobutyl ketone. Solutions of germanium prepared as described above had a total volume of about 2 ml. Other solutions were prepared by the same technique using a larger amount of ketone in the extraction of germanium from hydrochloric acid medium so as to have a final volume varying from 1 to 4 ml. This variation was found to have no apparent effect on the final result.

Effect of addition of different solvents to the reaction product. A number of solvents were substituted for ethyl alcohol to complete the volume of 10 ml after performance of the reaction in methyl isobutyl ketone with alcoholic phenylfluorone. Readings were taken against blanks prepared exactly in the same manner.

Comparative results reported in Table II were calculated on the basis of the measurements taken with the solutions completed with ethyl alcohol assumed to be correct for this particular purpose.

Table II. Effect of different solvents
μg Ge present in 10 ml: 1. 0.80; 2. 2.00

Solvents	μg Ge found		λ, nm
	1	2	
Ethyl alcohol	0.80	2.00	504
Methyl alcohol	0.80	2.00	502
Isobutyl alcohol	0.80	2.00	506
Methyl isobutyl carbinol	0.78	1.98	508
Ethylene glycol	0.79	1.90	504
Acetone	0.75	1.95	504
Methyl ethyl ketone	0.80	1.98	506
Methyl isopropyl ketone	0.80	2.00	504
Methyl isobutyl ketone	0.80	2.00	504
Isopropyl ether	0.80	2.00	508
Dioxane	0.77	1.90	504
Ethyl acetate	0.78	1.96	506
Benzene	0.73	1.85	508
Carbon tetrachloride	0.76	1.93	510

Since slight differences in spectral characteristics were noticed; the wave length of maximum absorption was chosen in every case.

Stability of color. In the range studied, of 0.02 to 0.50 μg Ge/ml (final dilution), spectrophotometric readings were found to be reproducible within 24 hours after exposure to ordinary light at room temperature. It was observed, however, that samples kept in the dark maintained their original absorption power even after two weeks. Effect of light on color stability is attributed to peroxide formation in the ketone which slowly interacts with phenylfluorone.

Spectral characteristics and sensitivity. In Fig. 1 the spectra of colored solutions in aqueous and organic media are compared and in Table III measurements taken at the wavelength of maximum absorption are reported. As may be seen the reaction is about twice as sensitive in organic solution.

Concentration range. A plot of the data according to Ringbom's[5] method indicates optimum concentration range to be 0.08 to 0.30 μg Ge/ml (final dilution).

Precision study. Results of two series of experiments of 20 independent determinations were taken to evaluate the precision of the method. As shown in Table IV the standard deviation for the first set was 0.0022 in terms of absorbance values and of 0.0025 for the second set. For a single measurement the probable errors were 0.0015 and 0.0017 respectively, which in terms of germanium concentration indicates that a single determination should be correct to $\pm$ 0.01 μg over the range studied.

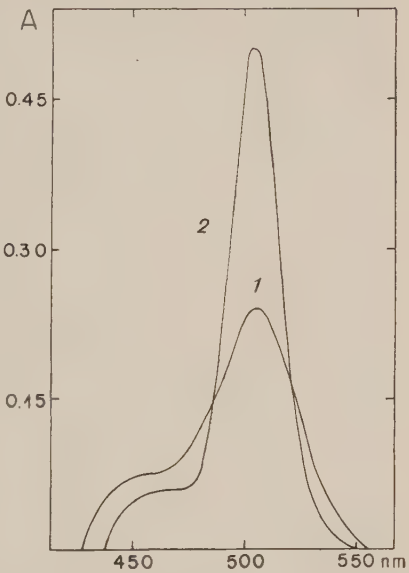

Fig. 1. Absorption spectra. Measurements taken against corresponding blanks. 0.20 μg Ge/ml. Curve 1; aqueous solution. Curve 2: methyl isobutyl ketone + ethyl alcohol

Nature of the colored solution. The mixed solvents system containing the reaction product showed general characteristics of a true solution including no Tyndall effect.

Table III. Determination of Ge in aqueous and organic medium
Absorbance at 504 nm

μg Ge/ml final dilution	Aqueous medium		Organic medium methyl isobutyl ketone + ethyl alcohol
	I	II	
0.02	—	—	0.054
0.05	0.051	—	0.131
0.08	0.097	0.086	0.204
0.10	0.120	0.123	0.255
0.20	0.242	0.244	0.496
0.30	0.372	—	0.736
0.40	0.492	0.456	0.967
0.50	0.625	—	1.252

I = Performed according to *H. J. Cluley*[3].
II = Performed according to *C. L. Luke* and *M. E. Campbell*[4].

In an attempt to elucidate the nature of this solution, it was found interesting to study the solubility properties of the germanium-phenylfluorone compound. Two preparations of this compound were made. The first in the manner described by *Stipanits* and *Hecht*[6], by starting from 20 mg of GeO_2 and the second by using an amount of phenylfluorone not sufficient to react with all the germanium present. In the latter case 100 ml of the reagent solution of phenylfluorone were added to a slightly acidic aqueous solution of 2.5 mg Ge in about 100 ml. The precipitate was allowed to settle overnight, filtered, washed with water and dried in a desiccator, first over $CaCl_2$ and finally over P_2O_5.

Table IV. Precision study

Absorbance at 504 nm

0.80 μg Ge in 10.0 ml

0.204	0.206	0.205	0.206	0.204	0.205	0.208	0.203	0.207	0.205
0.202	0.202	0.201	0.206	0.201	0.204	0.204	0.208	0.201	0.203

Average 0.204; Aver. dev. 0.0017; Standard dev. 0.0022; Prob. error 0.0015

2.00 μg Ge in 10.0 ml

0.495	0.498	0.495	0.491	0.491	0.490	0.495	0.490	0.495	0.492
0.495	0.499	0.501	0.494	0.494	0.495	0.495	0.494	0.498	0.492

Average 0.494; Aver. dev. 0.0020; Standard dev. 0.0025; Prob. error 0.0017

The germanium-phenylfluorone compound was found to be insoluble in a number of pure organic solvents, cf. [6], including methyl isobutyl ketone. It was observed, however, that it was appreciably soluble in methyl isobutyl ketone, methyl isopropyl ketone and methyl isobutyl carbinol previously saturated with hydrochloric acid 2 : 1, as well as in acetone, methyl and ethyl alcohol and ethylene glycol containing 10% concentrated hydrochloric acid.

Solutions of the compound were then prepared by dissolving definite amounts of the dry product, weighed on a micro-balance, in methyl isobutyl ketone saturated with 7.5 *N* HCl and the volume completed with ethyl alcohol.

Other solutions were also prepared by adding a measured excess of alcoholic phenylfluorone solution in order to attain exactly the same conditions as in the analytical procedure under study.

Comparison of the spectral characteristics of both series of solutions shows that the addition of excess phenylfluorone produces an intensification of the absorbance values in the region of approximately 490 to 550 nm leading to results that are in satisfactory agreement throughout the whole spectrum with those obtained by the analytical procedure if the concentration of germanium is calculated on the basis of the formula given by *Stipanits* and *Hecht*[6].

Interferences. Of the elements known to interfere when the reaction of germanium with phenylfluorone is carried out in aqueous solution[2,3] Ga, Ti, Sn(IV), As(III and V), Bi and Ta(V) were found not to interfere when germanium was determined in the presence of at least 200 times the element investigated.

Sn(II), Sb(V), Sb(III), Mo(VI), Fe(III) and Zr were eliminated by a preliminary extraction of the corresponding cupferrates in sulfuric acid medium as earlier described[1]. It is to be noted, however, that in order to attain quantitative elimination of molybdate, the solution should be at least 3.5 *N* in H_2SO_4.

In this study two sets of experiments were run by taking 0.80 and 2.00 μg Ge respectively and 200 μg of the tested element except in the case of Mo(VI) and Fe(III) whose amounts were increased up to 1000 μg and 5000 μg respectively.

Interferences of Nb(V) and W(VI) were prevented by a previous extraction with excess thiocyanate under the conditions described below. Since large amounts of thiocyanate were found to affect the color of phenylfluorone in organic solution, most of the excess thiocyanate was eliminated by successive additional extractions with pure solvent, to prevent it from being carried along with the extracted germanium.

The efficiency of the treatment proposed for the elimination of W(VI) and Nb(V) is shown by the results summarized in Table V which were evaluated by making use of a calibration curve obtained exactly in the same manner.

Table V. Interference Study

Volume of solution extracted: 1.0 ml*

Amount of each interference present: 200 μg

Interference	Ge present μg	Ge found μg	Interference	Ge present μg	Ge found μg
W(VI)	0.80	0.80, 0.81, 0.79	Nb(V), Ta(V), W(VI)	1.00	1.06, 1.08, 1.00
		0.80, 0.81			1.04, 0.98
	2.00	2.00, 2.00, 1.99		2.00	2.02, 2.00
Nb(V)	0.80	0.81, 0.80, 0.81	Nb(V), Ta(V), W(VI), Fe(III)	1.00	1.02, 1.04, 1.00
		0.80			0.99, 0.98, 1.00
	2.00	1.99, 2.00, 2.00			
		2.03, 2.05			
Nb(V), Ta(V)	0.80	0.81			
	2.00	2.00, 1.98, 2.01			

* The same degree of accuracy was attained in the extraction of 2.0 and 5.0 ml.

Calibration curve. In the preparation of calibration curves it was found that a very slight extraction of germanium occurred in the treatment with cupferron since absorptiometric readings of the final solutions containing the reaction product with phenylfluorone, although reproducible, were somewhat lower than expected. Fig. 2 shows a calibration curve plotted according to Ringbom.

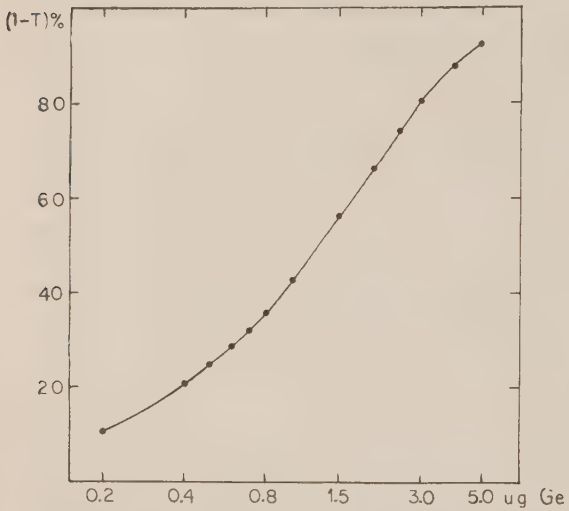

Fig. 2. Calibration curve. Ringbom's plot for 504 nm. The amount of germanium is that present in the aqueous phase

Reagent and Special Solutions

Phenylfluorone solution. Dissolve 0.050 g phenylfluorone in 200 ml of ethyl alcohol containing 12.5 ml of H_2SO_4 (1 + 6) on a water bath (70°). Let cool and bring volume to 250 ml with ethyl alcohol.

Standard germanium solution (stock solution), 1 mg Ge per ml. Dissolve 0.1441 g of pure GeO_2 in a minimum volume of 0.1 *M* sodium hydroxide and just acidify with dilute sulfuric acid. Dilute to 100 ml.

Standard germanium solution (working solution). Prepare freshly by proper dilution of stock solution.

Cupferron solution. Prepare freshly a saturated aqueous solution.

Ammonium thiocyanate solution. Prepare a solution containing 6 g of iron free ammonium thiocyanate per 10 ml.

Ascorbic acid solution. Prepare freshly a saturated aqueous solution.

Recommended General Procedure

1. To 1.0 ml of the sample solution, approximately 3.5 *N* in H_2SO_4, which should preferably contain 0.8 to 2.5 μg Ge, in a ground-stoppered test tube, add 0.1 ml of cupferron solution, 0.5 ml of methyl isobutyl ketone and shake. Wait a few seconds for phase separation. If any emulsion forms, centrifuge for a few seconds. Remove the ketone layer with an extraction pipet and discard it. Repeat extraction with three or four more additions of ketone using about 0.5 ml each time.

2. To the aqueous solution remaining from the preceding step add 1.0 ml of methyl isobutyl ketone and 2.0 ml of concentrated hydrochloric acid ($D = 1.18$). Shake vigorously. Wait a few seconds to allow for phase separation and remove the colorless organic layer, transferring it to a 10 ml volumetric flask. Repeat extraction twice by adding 0.7 ml of ketone each time to the aqueous solution.

3. To the combined extracts collected in the volumetric flask add 3.0 ml of reagent solution and make up to the mark with ethyl alcohol. Read transmittance at 504 nm against a blank run with all the reagents. Use a calibration curve prepared by the same procedure.

If the sample solution contains less than 0.8 μg Ge/ml take 2.0 to 5.0 ml instead of 1.0 ml and increase in a corresponding proportion the volumes of cupferron solution as well as of hydrochloric acid taken in steps 1 and 2 respectively. An additional extraction with 0.5 ml of ketone in step 1 is advisable.

If tungstate or niobium are present proceed as follows:

Tungstate present. After completing step 1 add 0.2 ml of ammonium thiocyanate solution if 1.0 or 2.0 ml of sample solution are taken in step 1 and increase addition proportionally up to 0.5 ml for a sample volume of 5.0 ml. Add also 0.1 ml of ascorbic acid solution per ml of aqueous solution and heat for 10 minutes in a water bath at 70–75°. Allow to cool for 10 minutes and extract with 0.5 ml of peroxide-free methyl isobutyl ketone. Discard the separated ketone layer and repeat extraction with five more additions of 0.5 ml of ketone. Carry out steps 2 and 3 as indicated.

Niobium present. Proceed as recommended in the presence of tungstate but after performing the first extraction with 0.5 ml ketone add 0.2 ml more of ammonium thiocyanate, heat again, let cool as indicated above and extract with at least 10 more additions of 0.5 ml of methyl isobutyl ketone. Perform steps 2 and 3 as usual.

Determination of Germanium in Complex Materials

Two synthetic mixtures, simulating flue dust, containing 0.040% Ge, whose compositions were reported in the first paper of this series[1] were analyzed for germanium. Approximately 0.1 g of sample were fused and desintegrated as previously indicated[1], but before adding sulfuric acid to dissolve the material in the volumetric flask, sodium tungstate and gallium nitrate solutions were added in sufficient amount to correspond to a percentage of 2.3 of WO_3 and 2.5 of Ga_2O_3 in the original mixtures. On account of the higher sensitivity of the method, aliquots of 1.0 ml instead of 5.0 ml were taken. Results obtained for mixture 1 and 2 were, respectively, 0.039, 0.040% and 0.040, 0.041% Ge.

Three different samples of coal were also analyzed by the same procedure. Fine pulverised material previously heated to constant

weight at 600° was used. About 0.150 g and 0.100 g of samples number 1 and 2 and 0.050 g of sample number 3 were taken in each determination.

The material was brought into solution in exactly the same way as described for the flue dust analysis and aliquots of 5.0 ml were always taken.

Parallel determinations were run in each case by adding a known amount of germanium to the original sample. As shown below results were found to agree very satisfactorily.

Table VI. Determination of germanium in coals, after ignition at 600°

Germanium content in 5.0 ml

Sample Nr.	Ge added μg	Ge found μg
1	none	2.37
	1.00	3.37
2	none	0.65
	1.00	1.64
3	none	2.22
	1.00	3.22

Remarks

The present study shows that the reaction of germanium with phenylfluorone can be carried out quantitatively, on the micro scale, in organic medium under suitable conditions and that as in the case of the molybdate reaction previously reported[1] the analytical procedure presents real advantages over the one performed in aqueous medium in spite of the important improvements introduced respectively by *Oka* and *Kanno*[7] and by *Luke* and *Campbell*[4] with regard to stability and time of color development*.

It seems worth mentioning the importance of the nature of the acid in the preparation of the reagent solution, although no clear explanation can be advanced for the present.

With regard to the slight extractability of germanium in the preliminary treatment with cupferron it is to be noted that this phenomenon was not observed in a previous work[1] by employing the same technique, because the amount of germanium extracted is so low that it fell out of the range of sensitivity of the method. In the present case, on the contrary, the method being about ten times as sensitive, losses of even such low concentrations can be detected.

Acknowledgement

Support given by the Rockefeller Foundation and the "Conselho Nacional de Pesquisas", Rio de Janeiro, Brazil, is gladly acknowledged. One of the authors *(L. S.)* is particularly grateful to the "Centro Técnico de Aeronautica", São José dos Campos, Brazil, and to the "Conselho Nacional de Pesquisas" for the grant of a fellowship.

* A recent paper of *Hillebrant* and *Hoste*[8] reached us while this manuscript was under preparation. The authors have succeeded in extracting the germanium phenylfluorone compound precipitated in aqueous medium by benzyl alcohol. The analytical procedure is about as sensitive as the one proposed in this paper.

Summary

Germanium extracted by methyl isobutyl ketone from 7.5 *N* hydrochloric acid solutions is made to react directly in the organic phase with phenylfluorone. Very stable colored solutions are obtained. The reaction is instantaneous and twice as sensitive as when carried out in aqueous medium with the same reagent. Optimum range of concentration for absorptiometric measurements was found to be 0.08 to 0.30 μg Ge/ml. Most of the interfering ions are separated by preliminary extraction of the cupferrates with the same ketone. W(VI) and Nb(V) are removed by previous extraction with excess thiocyanate in reducing medium making use of the same solvent. The procedure is applicable to the determination of germanium in coals.

Zusammenfassung

Germanium wird aus 7,5-n Salzsäure mit Methylisobutylketon extrahiert und unmittelbar in der organischen Phase mit Phenylfluoron umgesetzt. Die Reaktion erfolgt sofort, ist doppelt so empfindlich als in wäßriger Phase und führt zu sehr stabil gefärbten Lösungen. Die für Absorptionsmessungen am besten geeignete Konzentration liegt zwischen 0,08 und 0,30 μg Ge/ml. Die meisten störenden Ionen werden durch vorhergehende Extraktion ihrer Cupferonate mit demselben Keton entfernt. Wolfram(VI) und Niob(V) werden mit demselben Lösungsmittel in Gegenwart überschüssigen Rhodanids in reduzierendem Milieu abgetrennt. Das Verfahren eignet sich für die Bestimmung von Germanium in Kohle.

Résumé

On fait réagir directement le germanium avec la phénylfluorone, dans la phase organique, après son extraction par la méthylisobutylcétone de sa solution 7,5 *N* chlorhydrique. On obtient ainsi des solutions colorées très stables. La réaction est instantanée et deux fois plus sensible que lorsqu'elle est effectuée en milieu aqueux avec le même réactif. Le domaine de concentration optimum pour les mesures absorptiométriques est situé entre 0,08 et 0,30 μg Ge/ml. La plupart des ions gênants sont séparés par une extraction préalable des cupferrates par la cétone. W(VI) et Nb(V) sont éliminés au cours d'une extraction préalable en présence d'un excès de thiocyanate en milieu réducteur et dans le même solvant. La technique est applicable à la détermination du germanium dans les charbons.

Literature

[1] *P. Senise* and *L. Sant'Agostino*, Mikrochim. Acta [Wien] **1956**, 1445.
[2] *W. A. Schneider* and *E. B. Sandell*, Mikrochim. Acta [Wien] **1954**, 263.
[3] *H. J. Cluley*, Analyst **76**, 523 (1951).
[4] *C. L. Luke* and *M. E. Campbell*, Analyt. Chemistry **28**, 1273 (1956).
[5] *G. H. Ayres*, Analyt. Chemistry **21**, 652 (1949).
[6] *P. Stipanits* and *F. Hecht*, Z. analyt. Chem. **152**, 185 (1956).
[7] *Y. Oka* and *T. Kanno*, J. Chem. Soc. Japan, Pure Chem. Sect. **76**, 874 (1955); Sci. Rep. RITU, A-**7**, 396 (1955).
[8] *A. Hillebrant* and *J. Hoste*, Analyt. Chim. Acta **18**, 569 (1958).

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Papierscheiben-Säulenchromatographie

Von

L. Roth*

Mit 2 Abbildungen

(Eingegangen am 20. Januar 1959)

In der präparativen Chromatographie werden vorwiegend gestopfte Säulen verwendet, die auch bei sorgfältigem Arbeiten zu Schlieren- oder Rißbildung neigen. Ein Wechsel des Lösungsmittels sowie die Verwendung von Sprühreagenzien zur Erkennung der Substanz während des Betriebes ist praktisch nicht möglich.

Für die präparative Herstellung kleinerer Mengen chromatographisch reiner Naturstoffe wurde eine Methode gesucht, die die oben angeführten Nachteile nicht hat, schnell auszuführen ist und einen möglichst geringen Aufwand an Geräten erfordert.

Als geeignete Methode erwies sich die aufsteigende Chromatographie mit Säulen aus runden Scheiben von präparativem (dickem) Chromatographiekarton (Macherey u. Nagel Nr. 866).

Es wurde mit Scheiben von 25, 50 und 58 mm Durchmesser in den beiden nachstehend beschriebenen Geräten gearbeitet. Größere Scheiben und andere Geräte werden gegenwärtig noch erprobt.

Geräte zur Säulenchromatographie

Zur Befestigung des in Abb. 1 gezeigten Gerätes trägt ein Stativ *A* drei Klammern mit Muffen *B*. Die unterste Klammer hält einen Trichter mit geschliffenem Rand *C*; auf dem Trichter befindet sich eine am Rand mit einer Dichtung versehene Loch- oder Sinterplatte *D*, auf der die Säule aus runden Pappscheiben *E* aufgebaut wird. Diese Säule wird durch einen Stempel *F* mit mäßigem Druck zusammengepreßt. Während des Betriebes wird der Glaszylinder *G* über die Säule heruntergeschoben,

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um ein Verdunsten des Lösungsmittels möglichst zu vermeiden. Man erreicht einen gleichmäßigen Abstand der Säule von der Zylinderglaswand durch senkrechtes Einschieben von drei oder vier Glasstäben zwischen Säule und Zylinderwand. Das für die Entwicklung notwendige Lösungsmittel wird aus dem Vorratsgefäß *H* durch einen Schlauch zum Trichter *C* geleitet. Während des Betriebes werden Trichter und Glaszylinder durch zwei Klammern *J* zusammengehalten.

Das in Abb. 2 wiedergegebene Gerät ist nach ähnlichem Prinzip wie das oben beschriebene gebaut. Der Trichter *C* hat jedoch oben eine Schliffhülse und der Glaszylinder *G* unten einen Schliffkern. Die Loch- oder Sinterplatte *D* ist mit dem Trichter fest verschmolzen. Bei geringerem Durchmesser der Papierscheiben (25 mm) genügt es, wenn der Trichterrand eine ringartige Auflage hat. Bei größerem Durchmesser muß eine Loch- oder Sinterplatte an dieser Stelle eingefügt werden. Das Lösungsmittelgefäß *H* wird von unten angehoben, bis das Lösungsmittel das Niveau der Lochplatte *D* erreicht hat und die Papierscheiben das Lösungsmittel aufzusaugen beginnen. Die Säule hat während des Betriebes eine genügend große Saugfähigkeit, um das Lösungsmittel aufzusaugen, so daß das Lösungsmittelgefäß nicht weiter gehoben zu werden braucht.

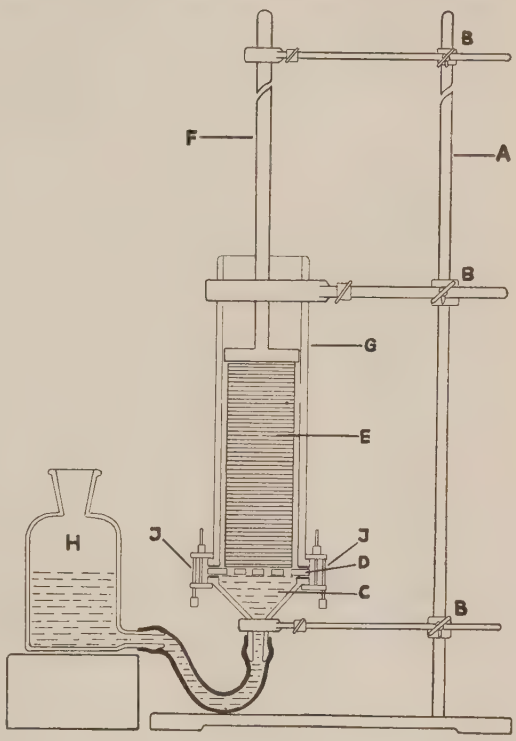

Abb. 1

Anwendungsbeispiele

Eine verunreinigte Substanz, die chromatographisch rein dargestellt werden soll, wird zuerst einem Probechromatogramm, das in der üblichen Weise auf Filtrierpapier entwickelt wird, unterworfen, um das für die vorgesehene Trennung günstigste Lösungsmittelgemisch auszuwählen. In vielen Fällen ist dieses Lösungsmittelgemisch schon bekannt. Eine

oder mehrere Pappscheiben werden mit einer konz. Lösung der Substanz getränkt und getrocknet. Auf die Lochplatte *D* werden nun zunächst zwei bis drei unbehandelte Scheiben, darüber die mit der Substanz getränkten Scheiben gelegt, darauf wird die Säule in der gewünschten Höhe aus Scheiben aufgebaut, durch den Stempel *F* leicht zusammengepreßt und in Betrieb genommen. Das Aufsteigen des Lösungsmittels kann man an dem Aufquellen der gestanzten Ränder der Pappscheiben gut verfolgen. Die anfänglich gehegte Befürchtung, daß das Lösungsmittel in der Säule verschieden schnell „laufen" würde, erwies sich als unbegründet; die festgestellten Differenzen der Laufgeschwindigkeit auf verschiedenen Seiten der Säule waren nicht größer als ein bis zwei Scheibenstärken (zirka 2 bis 4 mm). Um festzustellen, ob die Substanz in der Säule genügend von den Verunreinigungen getrennt ist, wird bei ungefärbten Substanzen der Zylinder *G* hinaufgeschoben und entweder die Säule mit einer geeigneten Reagenslösung angesprüht, oder es werden einige Pappscheiben aus der Säule entnommen, mit denen dann die notwendigen Reinheitsprüfungen vorgenommen werden. Durch dieses Verfahren kann man auch, namentlich bei Stoffen, die in geringem Abstand in der Säule vorhanden sind oder sich teilweise überdecken, feststellen, in welchem Teil der Säule der gewünschte Stoff chromatographisch rein enthalten ist. Durch eine kleine Presse, wie sie zum Auspressen von halben Zitronenscheiben gebräuchlich sind, kann man aus einem in der Mitte zusammengefalteten Pappscheibchen einige Tropfen auspressen, von denen man zur Reinheitsprüfung in der üblichen Weise auf einem Papierbogen ein Probechromatogramm anfertigt. Diejenigen Pappscheiben, die den gewünschten Stoff rein enthalten, werden aus der Säule entnommen und getrocknet. Die chromatographisch reine Substanz wird daraus auf einer Filternutsche oder im Soxhlet-Apparat eluiert.

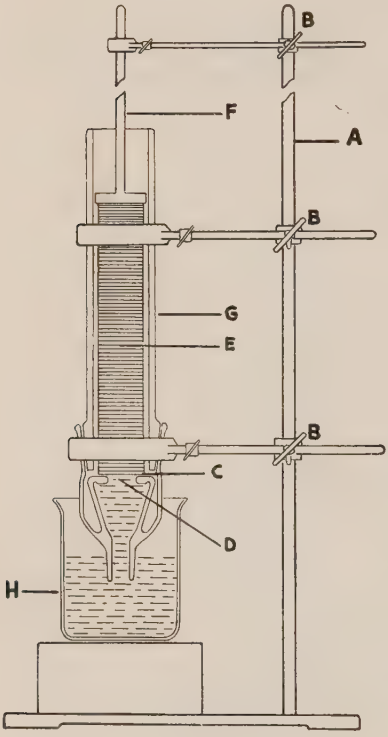

Abb. 2

Erweist sich eine Säule während des Betriebes als zu kurz, oder soll zur besseren Trennung zweier Stoffe noch weiter entwickelt

werden, so kann man die Säule beliebig durch Auflegen neuer Scheiben verlängern.

Bei zwei sich überdeckenden Fraktionen ist es möglich, durch Einbringen der Pappscheiben, die diese Stoffe enthalten, in eine neue Säule und durch Wechsel des Lösungsmittels einen ähnlichen Effekt zu erzielen wie durch die zweidimensionale Papierchromatographie. Durch vorheriges Wägen und Markieren einer bestimmten Anzahl gut getrockneter Pappscheiben, die in einer vorausbestimmten Höhe in die Säule eingefügt werden, und „Hineinentwickeln" des gewünschten Stoffes in die gewogenen Pappscheiben, anschließendes Trocknen und nochmaliges Wägen kann ein Stoff auch quantitativ bestimmt werden.

Zusammenfassung

Durch Säulen aus Filtrierkarton kann in aufsteigender Chromatographie eine Substanz von störenden Begleitstoffen befreit werden. Es ist möglich, während des Betriebes durch Sprühreagenzien Feststellungen über die Lage des Stoffes in der Säule zu machen oder — bei kurzer Unterbrechung — mit einzelnen Scheiben Reinheitsprüfungen durchzuführen. Die Säule kann während des Betriebes verlängert werden. Eine quantitative chromatographische Bestimmung ist möglich.

Summary

A substance can be freed of interfering accompanying materials by ascending chromatographing in columns made of filtering paperboard. It is possible, during the operation, to locate the materials in the column by sprayed-on reagents or—with brief interruption—to conduct purity tests with individual disks. The column can be lengthened during the operation. It is possible to make a quantitative chromatographic determination.

Résumé

Il est possible de purifier une substance de produits gênants l'accompagnant par chromatographie ascendante sur des colonnes en carton filtre. Il est possible de se rendre compte de la position de la substance pendant l'opération à l'aide de réactifs pulvérisés et également après une courte interruption d'effectuer des essais de pureté sur des disques isolés. Pendant l'opération, il est possible d'allonger la colonne. Il est également possible d'effectuer une détermination chromatographique quantitative.

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The Spectrophotometric Determination of Germanium with Phenylfluorone

By

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(Received January 27, 1959)

The analytical chemistry of germanium has been the subject of several review articles[1–3]. Recent developments in this field have mainly arisen from the introduction by *Cluley*[4] of phenylfluorone as a sensitive and selective reagent for the absorptiometric determination of germanium. Subsequent workers have adopted his use of a hydrochloric acid medium for the determination. Whilst the use of this medium facilitates the determination after a separation by distillation of germanium tetrachloride, *Cluley*'s work indicates that in some respects sulphuric acid is a more suitable medium for the colour development.

The present paper describes the development of a method which has been applied to the determination of germanium, after a separation by solvent extraction, in a wide range of rocks, minerals, sediments and sea-water samples[5]. Ethylenediaminetetra-acetic acid (E. D. T. A.) has been used to suppress the interfering effects of some elements in the spectrophotometric procedure, its use for this purpose has been briefly discussed by *Luke* and *Campbell*[6].

Spectrophotometric Determination of Germanium

The effect of variations in the concentration of phenylfluorone on the formation of the germanium-phenylfluorone complex, was investigated in an attempt to reduce the high absorbancies at 520 nm of the blank solutions obtained with the amounts of reagents recommended by *Cluley*[4], for colour development in a sulphuric acid medium.

Solutions containing 20 μg of germanium were treated with 5 ml of 0.5% gum arabic solution, 10 ml of 14.3% *v/v* sulphuric acid and various

amounts of 0.05% phenylfluorone reagent (prepared as in the recommended method). Ethyl alcohol was added to maintain the volume of alcohol at 15 ml in each determination, and the solutions were diluted to 50 ml with water. Blanks, omitting the germanium, were similarly treated. The optical densities of the solutions were measured at intervals in 1-cm cells at 520 nm. The results (Table I) indicated that the use of 3 ml of

Table I. Effect of phenylfluorone concentration on colour development

Volume of phenylfluorone solution, ml	Optical density (less blank) at 520 nm			
	After 30 mins.	90 mins.	2 hours	3 hours
2	0.154	0.279	0.310	0.333
3	0.331	0.363	0.372	0.371
4	0.355	0.364	0.373	0.376

0.05% phenylfluorone solution reduced the blank value by half and gave a substantially complete colour development within two hours. This amount of reagent was used in subsequent work.

In similar experiments the amount of 0.5% gum arabic solution was varied (Table II). As a result of these experiments, in subsequent work the amount of gum arabic was reduced to 0.5 ml of 0.5% solution, with a slight increase in the sensitivity of the method.

Table II. Effect of gum arabic concentration on colour development

Volume of gum arabic solution, ml	Optical density (including blank) at 520 nm		
	After 60 mins.	120 mins.	150 mins.
0.5	0.421	0.459	0.460
1.0	0.393	0.430	0.432
2.0	0.378	0.412	0.411
3.0	0.375	0.403	0.409

The effect of E.D.T.A. on the reaction was next examined. Water samples containing 10 μg of germanium and various amounts of a 1% solution of the disodium salt of E.D.T.A. were treated by the recommended procedure. Blanks, omitting the germanium, were also run. The results (Table III) show that although the presence of E.D.T.A. retards the colour formation, the reduction in optical density is less than 3% with 0.02% of the complexing agent. Increase in the E.D.T.A. concentration was followed by a sharper decrease in sensitivity and with 2% of the complexing agent a precipitate was formed in the solution.

Table III. Effect of E. D. T. A. on colour development

Amount of E. D. T. A. solution ml	Optical density		
	Blank	Determination (10 μg Ge)	Difference
0	0.036	0.452	0.416
0.5	0.034	0.439	0.405
1.0	0.035	0.405	0.370
2.0	0.037	0.378	0.341
3.0	0.039	0.348	0.309
4.0	0.044	0.325	0.281

Beer's Law

Replicate determinations of various amounts of germanium were made in order to investigate the range over which Beer's law was obeyed. The mean deviations of the results obtained at each concentration ranged from 0.4 to 1.2% (mean 0.7%). Adherence to Beer's law was found in the range 0.1 to 0.6 p. p. m. At lower concentrations, which were investigated using a 4-cm cell, Beer's law was not obeyed and the sensitivity of the method decreased sharply with a decrease in the germanium concentration, indicating that the determination of very small amounts of germanium could only be achieved by the addition of 0.05 p. p. m. of germanium to each determination and to the corresponding blank solution.

Method

Measurements of optical density were made with a Unicam S. P. 500 spectrophotometer, against distilled water in the compensator cell.

Reagents

Sulphuric acid, 14.3% v/v. Dilute 60 ml of concentrated sulphuric acid to 420 ml.

Phenylfluorone reagent. Dissolve 0.05 g of phenylfluorone in 75 ml of ethyl alcohol and 5 ml of 14.3% *v/v* sulphuric acid by warming on the water-bath. Dilute the cooled solution to 100 ml with ethyl alcohol.

E.D.T.A. solution. Dissolve 1 g of the disodium salt of ethylenediaminetetra-acetic acid in water and dilute to 200 ml.

Gum arabic solution. Dissolve 0.1 g of gum arabic in ca. 80 ml of boiling water. Filter the solution and dilute to 100 ml.

Standard germanium stock solution (100 μg Ge/ml). Weigh out 0.0360 g of "Specpure" germanium dioxide and shake gently with 0.5 g of sodium hydroxide and 20 ml of water until the solution is complete. Dilute to 250 ml.

Standard germanium dilute solution (5 μg Ge/ml). Prepare as required by dilution of the stock solution.

Ethyl alcohol.

Determination of Germanium

To the test solution, contained in a 25-ml graduated flask, add 5 ml of 14.3% sulphuric acid, 1 ml of E.D.T.A. solution, 6 ml of ethyl alcohol, 1 ml of gum arabic solution and 1.5 ml of phenylfluorone reagent. Dilute to 25 ml with water and after two hours measure the optical density at 520 nm (the cell length may be from 1 cm to 4 cm depending on the germanium concentration). Determine the reagent blank in a similar manner, omitting the sample. Prepare a calibration curve using the standard germanium dilute solution. In determining small amounts of germanium, sample solutions, blanks and standards must be treated with 2.5 μg of germanium (i. e. 0.5 ml of the standard germanium dilute solution) to bring the determination within the range in which Beer's law is obeyed.

Interferences

The possible interfering effects of a number of elements were investigated by carrying out determinations of 10 μg of germanium in the presence of each of these elements. Determinations were also performed under the same conditions, but in the absence of added germanium. Similar experiments were made in the presence of 1 ml of 0.5% E.D.T.A. solution.

Table IV. Effect of E.D.T.A. on the interferences of certain elements

Element	Added as	Amount of element μg	Optical density at 520 nm					
			No E.D.T.A. added			E.D.T.A. added		
			No Ge	10 μg Ge	Difference	No Ge	10 μg Ge	Difference
—	—	—	0.036	0.452	0.416	0.034	0.439	0.405
Antimony	Antimony trichloride	20	0.076	0.510	0.434	0.042	0.477	0.435
Arsenic	Sodium arsenate	20	0.033	0.472	0.439	0.031	0.435	0.404
Arsenic	Sodium arsenite	20	0.042	0.474	0.432	0.035	0.442	0.407
Gallium	Gallium caesium alum	20	0.049	0.481	0.432	0.036	0.444	0.408
Indium	Indium chloride	10	—	—	—	0.034	0.443	0.409
Iron	Ferric alum	500	—	—	—	0.044	0.454	0.410
Iron	Ferric alum	1000	—	—	—	0.053	0.473	0.420
Molybdenum	Ammonium molybdate	20	0.069	0.512	0.443	0.046	0.466	0.420
Tellurium	Potassium tellurate	10	—	—	—	0.034	0.438	0.404
Thallium	Thallous nitrate	10	—	—	—	0.035	0.440	0.405
Tin	Stannous chloride	20	0.186	0.580	0.394	0.033	0.440	0.407

The results (Table IV) show the value of E.D.T.A. in suppressing the interfering effects of certain elements. The suppression of the interference of stannous tin and the high sensitivity of phenylfluorone as a reagent for this element in the absence of E.D.T.A., should make possible the determination of germanium and tin when present together, without a preliminary separation from each other.

The interference of antimony could not be completely suppressed, using E.D.T.A., but it was found that the addition of 1 ml of 1% citric acid to the determination, completely eliminated the interference from 20 μg of antimony, whilst having no significant effect on the colour from germanium.

Summary

A procedure is described for the spectrophotometric determination of germanium using phenylfluorone in a sulphuric acid medium. The amounts of phenylfluorone and gum arabic used are lower than have hitherto been employed, and lead to a lower reagent blank and slightly increased sensitivity. Ethylenediaminetetra-acetic acid is used to suppress the interfering effects of some elements and germanium may be determined in the presence of at least an equal concentration of antimony, arsenic, gallium, indium, tellurium, thallium and tin. In the presence of a fiftyfold excess of ferric iron the error in the determination of germanium is ca. 2%. Beer's law is obeyed in the range 0.1 to 0.6 p. p. m. of germanium.

Zusammenfassung

Eine spektrophotometrische Bestimmung des Germaniums mit Phenylfluoron in schwefelsaurer Lösung wurde beschrieben. Die verwendeten Mengen Phenylfluoron und Gummi arabicum sind geringer als bisher üblich, so daß der Blindwert geringer und die Empfindlichkeit größer ist. AEDTA dient zur Unterdrückung störender Einflüsse einiger Elemente, so daß Germanium auch in Gegenwart gleicher Mengen von Sb, As, Ga, In, Te, Tl und Sn bestimmt werden kann. Bei Anwesenheit eines 50fachen Überschusses an Eisen(III) beträgt der Fehler der Bestimmung etwa 2%. Das Beersche Gesetz ist zwischen 0,1 und 0,6 p. p. m. Ge erfüllt.

Résumé

Description d'une technique de dosage spectrophotométrique du germanium à l'aide de la phénylfluorone en milieu acide sulfurique. Les quantités de phénylfluorone et de gomme arabique employées sont plus faibles que celles que l'on avait utilisées jusqu'ici et elles permettent d'obtenir une correction d'essai à blanc de réactif également plus faible ainsi qu'une sensibilité légèrement accrue. On emploie l'acide éthylènediaminetétra-acétique pour supprimer les effets gênants de quelques éléments de sorte qu'il est possible de doser le germanium en présence d'antimoine, d'arsenic, de gallium, d'indium,

de tellure, de thallium et d'étain à des concentrations au moins égales à la sienne. En présence d'une quantité d'ions ferriques 50 fois plus élevée que celle du germanium, l'erreur de dosage de ce dernier est d'environ 2%. La loi de *Beer* est respectée dans un domaine compris entre 0,1 à 0,6 p. p. m. de germanium.

Literature

[1] *F. Hecht* and *G. Barthelmus*, Mikrochem. **36/37**, 466 (1951).
[2] *H. H. Krause* and *O. H. Johnson*, Analyt. Chemistry **25**, 134 (1953).
[3] *H. Oikawa*, J. Coal Res. Inst., Japan **5**, 140, 166, 203, 238, 298 (1954).
[4] *H. J. Cluley*, Analyst **76**, 523 (1951).
[5] *J. D. Burton* and *J. P. Riley*, Geochim. Cosmochim. Acta. In the Press.
[6] *C. L. Luke* and *M. E. Campbell*, Analyt. Chemistry **28**, 1273 (1956).

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Die Bestimmung des Kupfers in Blutserum mit Bleidiäthyldithiocarbaminat

Von

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(Eingegangen am 9. Januar 1959)

Für die Bestimmung des Kupfers in Blutserum scheint die kolorimetrische Methode von *Callan* und *Henderson*[1] sehr verbreitet und gut anwendbar zu sein. Der sich mit dem Natriumsalz des Diäthyldithiocarbaminates (DDC) bildende farbige Komplex ist die Grundlage dieses Verfahrens. Das Reagens wurde später auch mehrfach für die kolorimetrische Bestimmung des Serumkupfers verwendet[2–5].

Na-DDC gibt auch mit anderen Metallen farbige Komplexe. Bei der Bestimmung des Kupfers in Serum macht hauptsächlich die störende Wirkung des Eisens Schwierigkeiten. Nach der Meinung von *Šedivec* und *Vašák*[6] läßt sich die Selektivität der Kupferreaktion verbessern, indem man anstatt des Natriumsalzes das Bleisalz verwendet. Die Reaktion verläuft nach der Gleichung:

$$Pb(DDC)_2 + Cu^{2+} = Cu(DDC)_2 + Pb^{2+}.$$

Bei der Extraktion mit Chloroform gehen nur die Komplexe des Silbers und des Quecksilbers(II) in die Chloroformphase über. Deren Farbintensität ist aber so gering, daß sie die Bestimmung des Kupfers nicht stört. Die Reaktion ist quantitativ und der Kupferkomplex kann aus der wäßrigen Phase leicht ausgeschüttelt werden. Cd(II), Ni(II), Fe(III), Zn(II), As(V) und Tl(I) stören nicht, weil sich deren Komplexe in der Wasserphase leichter lösen als der Bleikomplex.

Die Bestimmung von Kupferspuren in Wasser mittels $Pb(DDC)_2$ haben *Kovařik* und *Vinš*[7] ausgearbeitet. Die beiden Autoren haben festgestellt, daß noch 0,02 μg Cu/ml gut bestimmt werden können. Bei der Analyse natürlicher Wässer stören 0,1 g Bleinitrat, 0,1 g Zinknitrat,

0,1 g Eisennitrat, 0,1 g Calciumnitrat, 0,1 g Magnesiumnitrat, 0,1 g Mangannitrat und 1 mg Nickelnitrat die Bestimmung des Kupfers nicht. $Pb(DDC)_2$ schien daher auch für die Bestimmung des Kupfers in Blutserum anwendbar zu sein.

Zunächst haben wir die Löslichkeit des Kupferkomplexes in organischen Lösungsmitteln untersucht und dabei festgestellt, daß er in n-Butanol und in i-Amylalkohol besser löslich ist als in Chloroform. Wir führen die Extraktion daher mit n-Butanol durch und sehen, daß einmaliges Ausschütteln praktisch hinreicht, da schon die Extinktion der zweiten Ausschüttelung mit der des reinen Lösungsmittels (0,05) übereinstimmt.

Reagenzien

Lösung von $Pb(DDC)_2$ in n-Butanol: zu deren Herstellung haben wir die Vorschrift von *Šedivec* und *Vašák* etwas abgeändert; wir lösen zunächst 0,05 g Bleiacetat p. a. in Wasser auf und setzen 2,5 ml 10%ige Seignettesalzlösung zu. Das Gemisch wird mit 2-n Kalilauge bis zur alkalischen Reaktion versetzt. Um Kupfer- und Eisenspuren zu maskieren, geben wir 2,5 ml n-Kaliumcyanidlösung zu und fällen mit einer wäßrigen Lösung von 0,06 g Na(DDC). Der Niederschlag wird mit einem Jenaer G 4-Filter abfiltriert, mit dest. Wasser gewaschen und sodann in n-Butanol gelöst. Die Lösung wird mit n-Butanol auf 500 ml aufgefüllt. Das Reagens hält sich in einer braunen Glasflasche ein Jahr.

Destillierte Salzsäure, 20%ig;

Trichloressigsäure p. a., 20%ig;

p-Nitrophenol, 1%ige, alkoholische Lösung;

Ammoniak p. a., 15%ig;

Schwefelsäure p. a., 0,5-n;

Komplexon III, p. a., 2,5%ige, wäßrige Lösung;

Kupferstammlösung: 1 g Elektrolytkupfer wird in 20 ml 6-n Salpetersäure gelöst, die Lösung auf dem Wasserbad zur Trockne eingedampft und der Rückstand in 1 l 0,1-n Salzsäure gelöst. Diese Stammlösung wird hundertfach verdünnt.

Durchführung der Bestimmung

1 ml Serum wird mit 6 ml bidest. Wasser verdünnt, mit 1 ml 20%iger Salzsäure versetzt und 10 Minuten stehen gelassen. Dann werden 2 ml 20%ige Trichloressigsäure zugegeben. Nach weiteren 10 Minuten wird filtriert. 5 ml Filtrat werden mit 1 ml 2,5%iger Komplexonlösung und einem Tropfen p-Nitrophenollösung versetzt. Man neutralisiert mit Ammoniak bis zur Gelbfärbung und säuert mit 0,5-n Schwefelsäure bis zum Verschwinden der Farbe an. Dann schüttelt man mit 5 ml DDC-Reagens aus. Die Messung erfolgt in einer Kleinküvette bei 5 cm Schichtdicke unter Vorschalten des Filters S 43 im Pulfrich-Photometer.

Unter Verwendung bekannter Kupfermengen (0,5, 1, 3 bzw. 5 μg) anstelle des Serums wird nach der angegebenen Arbeitsvorschrift eine Eichkurve ermittelt. Als Vergleichslösung dient eine Blindprobe. Bei Verwendung von Mikroküvetten kann man auch von 0,5 ml Serum ausgehen.

Durch Zusatz bekannter Kupfermengen zum Serum haben wir die Anwendbarkeit des Verfahrens geprüft. Die erhaltenen Werte sind in Tabelle 1 angeführt und zeigen, daß $Pb(DDC)_2$ als Reagens zur Kupferbestimmung in Serum gut geeignet ist.

Tabelle 1

μg Cu/ml Serum	μg Cu/ml zugegeben	μg Cu/ml gefunden	Δ %
1,5	0,15	1,7	+ 3
1,55	2,00	3,65	+ 2,8
1,55	1,00	2,6	— 1,9
1,45	0,5	1,9	— 2,6
1,45	1,00	2,35	— 4
1,25	1,00	2,3	— 2,2
1,7	0,5	2,25	+ 2,3

Um festzustellen, ob vor allem das im Blutserum vorhandene Eisen die Bestimmung des Kupfers stört, haben wir die in verschiedenen Serumproben ermittelten Kupferwerte nach Zusatz von Eisen nochmals bestimmt. Die in Tabelle 2 wiedergegebenen Werte lassen erkennen, daß auch die Anwesenheit der zehnfachen Eisenmenge keine wesentliche Störung verursacht. Auch mehrfache Mengen der im Serum enthaltenen Metalle Na, K, Ca und Mg und der Spurenelemente Zn, Pb, Al und Mn stören nicht.

Tabelle 2

μg Cu/ml Serum	μg Fe/ml zugegeben	μg Cu/ml gefunden	Δ %
1,5	6,00	1,55	+ 3,3
1,45	12,00	1,55	+ 6,8
1,55	12,00	1,95	+ 8
1,55	12,00	1,6	+ 3,2
1,55	6,00	1,65	+ 6,4
1,45	12,00	1,45	± 0
1,55	18,00	1,7	+ 9,6

Zusammenfassung

Anstelle des zur Kupferbestimmung in Serum vielfach angewendeten Natriumdiäthyldithiocarbaminates verwenden wir eine Lösung von Bleidiäthyldithiocarbaminat in n-Butanol. Der Vorteil dieser Modifikation

ist einerseits die geringe Menge des erforderlichen Untersuchungsmaterials, anderseits die Stabilität des Reagens. Das Verfahren ist für Serienuntersuchungen geeignet. Noch 0,3 μg Kupfer/ml sind gut bestimmbar. Eisen und auch die anderen im Serum vorhandenen Kationen stören die Reaktion nicht.

Summary

The writers use a solution of lead diethyldithiocarbamate in *n*-butanol in place of the sodium diethyldithiocarbamate widely used for the determination of copper in serum. The advantage of this modification is twofold: 1. the slight amount of the test material required and 2. the stability of the reagent. The procedure is suited for series investigations. As little as 0.3 μg of copper/ml can be determined satisfactorily. Iron as well as the other cations present in the serum do not interfere with the reaction.

Résumé

Emploi d'une solution de diéthyldithiocarbamate de plomb dans le *n*-butanol au lieu du diéthyldithiocarbamate de sodium, le plus souvent employé, pour la détermination du cuivre dans le sérum. L'avantage de cette modification est d'une part la faible quantité nécessaire de la substance à analyser et d'autre part la stabilité du réactif. Le mode opératoire est approprié aux déterminations en série. Il est encore possible de déterminer correctement 0,3 μg/ml de cuivre. Le fer et les autres cathions également présents dans le sérum ne perturbent pas la réaction.

Literatur

[1] *T. Callan* und *J. A. R. Henderson*, Analyst **54**, 650 (1929).
[2] *W. D. McFarlane*, Biochemic. J. **26**, 1022 (1932).
[3] *S. L. Tompsett*, Biochemic. J. **28**, 1544 (1934); **28**, 2088 (1934).
[4] *H. G. Schmidt*, Biochem. Z. **302**, 256 (1939).
[5] *J. C. Robinson*, J. Biol. Chemistry **179**, 1103 (1949).
[6] *V. Sedivec* und *V. Vašák*, Coll. trav. chim. Tchécoslovaquie **15**, 260 (1950); zitiert nach Z. analyt. Chem. **134**, 205 (1951/52).
[7] *M. Kovařik* und *V. Vinš*, Z. analyt. Chem. **147**, 401 (1955).
[8] *B. Flaschenträger* und *E. Lehnartz*, Physiologische Chemie, Bd. II/A. Berlin-Göttingen-Heidelberg: Springer-Verlag. 1954. S. 390.

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Mechanism and Elimination of Interferences in Flame Photometry*

Experimental Methods of Investigation and Suppressing Effects of Aluminium, Borate, Phosphate, and Sulphate on Calcium Radiation

By

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With 22 Figures

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Introduction

In the last decade the flame photometric method of determination has become an indispensable tool of chemical analysis, especially where alkali metals and alkaline earth metals are to be determined.

However, a serious drawback cannot be denied in that the radiation intensity of a specified element is not solely determined by the concentration of that element in a sample solution, but is generally affected by the nature and the concentration of some concomitants occuring in that solution. And in such a case, the result would be erroneous, unless some appropriate measure against interference is taken, which may sometimes need very tedious procedures and a long analysis time.

Extensive research efforts have been devoted to find adequate measures for the various kinds of interferences, and among them the most orthodox way of investigation must be to eliminate the interferences by setting up conditions which have been found, through the analysis of the mechanism of the interferences, to be free from them: As a typical example, *Pungor* et al.[1] found that mutual interferences between potassium, rubidium, and caesium are caused by the mechanism of ionization, which increases with the temperature of the exciting flame, and they succeeded

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in eliminating the interference by lowering the flame temperature below 1000° C.

In many cases, however, such an orthodox investigation does not seem feasible, because the experimental method of approach to the mechanism of an interference is generally poor.

Here I have developed two experimental methods of investigation into the mechanism of interferences, *the Separate Atomization Method*, and *the Location Dependence Method*, by which the process in which the interference of a concomitant occurs can be specified on an experimental basis.

By the use of these new methods the mechanisms of the well-known suppressing effects of aluminium, borate, phosphate and sulphate on calcium radiation, have been analysed and a remedy for these interferences has been suggested.

The suppression of the radiations of alkaline earth metals by aluminium, borate, phosphate and sulphate has attracted the author's attention, since the interferences of these four concomitants were found to be very similar to each other and were among the most remarkable exceptions to the general rule (Log-Log Translation Rule) of multiplicative interferences, when a comprehensive survey of the interference-phenomena was carried out[2].

Moreover, in the field of applied chemical analysis, the troubles caused by those interferences are sometimes really serious; hence, the elimination of them, if possible, seems to be of great practical value and significance.

Historical Considerations

In the literature numerous descriptions of the interference of aluminium and phosphate with alkaline earth radiations have already appeared: In 1933 *Child*[3] described the quenching of calcium and strontium radiations by addition of aluminium salts and he explained the effect of added salt by the possible effect of the equilibria in flame gases in which the alkaline earth element participates. *Mitchell* and *Robertson*[4] made reference to the same interference and attributed the quenching to absorption of the exciting energy by aluminium atoms in the flame.

Their explanations cited above seemed to lack concrete experimental proof and logical consideration. *Huldt*[5] first provided an experimental basis for the investigation into the mechanism of the interference: With a systematic postulation of the processes involved in the flame excitation, he assumed some possible resistance to the chemical equilibria in the gaseous phase between calcium atoms in the excited and the ground state, and in order to prove this mechanism he made a comparison of the "line-reversal temperature" of C_2H_2/air flames colored by calcium with and without addition of aluminium salt. The result, however, indicated no change in the flame temperature, that is, no change in Ca*/Ca abundance ratio (the ratio of the number of atoms in the excited level to that of atoms in the ground level), and moreover there was no spectral indication of a possible formation of some new compound between calcium and aluminium in the gaseous phase.

Török[6] described a stoichiometric relation between the concentration of alkaline earth element and the minimal concentration of phosphate which gives the maximum suppression, showing, in other words, that the radiation intensity of the alkaline earth element decreases sharply with increasing concentration of phosphate ion, but once a certain critical concentration of phosphate is exceeded no further decrease in intensity of the radiation takes place. This fact, confirmed later by *Köhnlein* and *Lücke*[7] and also by many other investigators, would justify speculation about the formation of a compound which might be excited only with difficulty in the flame, although there has been much confusion regarding "the composition of the compound". The meaning of "difficulty of excitation" has been argued variously by many authors: *Leyton*[8] and *Ikeda*[9] assumed the difficult dissociation of a chemical compound formed between calcium and phosphorus, i. e., the decrease of the light-emitting species of calcium through a chemical equilibrium in the flame, but their experimental basis is not obvious in respect of the stoichiometric relation between calcium and phosphate.

Tsuchihashi and *Sekido*[10] made comprehensive experiments and concluded that the suppressing effect of phosphate on calcium radiation has no relation to the variation in any property of the sample solution, e. g., p_H, viscosity, formation of complex ions in solution, so that the effect had to be attributed to some other cause in "the gaseous phase". On the other hand they could not recognize any spectral indication of the formation of a compound between calcium and phosphorus in hot flame gas, which agreed with the result obtained by *Leyton*[8].

Margoshes and *Vallee*[11] suggested difficulty of evaporation as the reason for the difficulty of exciting the compound formed on the addition of the interfering concomitants. They pointed out as the proof of this that a crystal of some calcium salts with high melting point (therefore possibly with high boiling point), being held in the hottest part of Bunsen or Meker flame, retains rather weak calcium-radiation for a relatively long period, and that aluminate, phosphate, sulphate etc. of calcium may belong to this category of compounds.

Some, but less, analogous information has been given in the literature[9,11,12] about the effect of sulphate.

Due to the lack of more direct experimental proof, however, these pieces of known facts and theoretical speculations have not yet been unified to a complete and systematic understanding of the mechanism, so that no effective method of elimination of those interferences has been known except the chemical separation of the interfering concomitants from the sample solution.

Theoretical Considerations

In the majority of recent flame photometers on the market, there are two different types of atomizer and burner system. One type is the so-called atomizer-burner unit which works with a turbulent flame. In this system the sample solution is directly injected amidst the turbulent flame. The other type is the ordinary Meker burner with separate atomizer. In this, the sample solution is atomized in a separate atomizer and only a limited portion of the finer mist is introduced into a silent laminar flame of the Meker type.

For this study the latter system has been preferred, because for a turbulent flame the stages of the flame reaction cannot be specified at each location of a flame and this feature of the atomizer-burner system seems to exaggerate the complexity of the phenomena.

The following theories may be applied to cases of a laminar flame with indirect atomization, but similar ones may be applicable to the other case with an atomizer-burner system.

a) Processes Involved in Excitation by Flame and Factors Influenced by Concomitants

In order to discuss the mechanism of the interferences in flame photometry, we must define all the processes involved in a series of physical changes and chemical reactions by which a specified element is led by excitation to emit a characteristic radiation in flame.

In the following arguments these processes may be conveniently divided into several stages, and for each one of these processes, various factors may be considered together with the possibility of their being influenced by concomitants.

Atomization Process: The sample solution, being sucked through a capillary, is atomized into fine droplets by the jet stream of compressed air or oxygen at the tip of the atomizer. The droplets are of various sizes. The major portion of the larger droplets are deposited upon the various parts of the atomizer wall and finally drained away, so that only a minute portion of the finer droplets is effectively introduced into the flame to contribute to further processes.

Various physical properties of a sample solution, i. e., density, viscosity, surface tension, etc. may be determinative factors for the speed of suction and the drop size distribution. When these factors are altered by concomitants, some variation in the rate of effective feed of the specified element into the flame and a consequent change in the emission intensity of the characteristic radiation may be effected.

Vaporization and Successive Rate Process: Fine droplets of the solution are carried by the gas stream into the flame. During a relatively short time of passage through the hot gases, solvent is evaporated off and liquid droplets may turn into fine solid particles of the solute salts. Finally, components of the solid particles, including the specified element and other concomitants, vaporize to enter into the gaseous phase.

The nature of chemical combination and the state of aggregation in the solid particles seem to be important rate-determining factors in vaporization. And these chemical and physical states must have a close relation to the total composition of the initial solution. Thus, the formation of a nucleus of the first precipitate during evaporation of the solvent may depend upon the solubility of the solutes involved, and the solid

particle may be porous, when a component is thermally decomposed to evolve gas or easily transformed from one crystalline form to the other. Some concomitant may combine with the specified element to form a compound which can be vaporized only with difficulty; or a concomitant may hinder the formation of such compounds and promote the vaporization of a specified element.

The light-emitting species of a specified element may sometimes be obtained directly by vaporization of the solid, but in other case by dissociation of a gaseous compound or combination with some other component in the gaseous phase. The occurence of these processes may depend on the chemical form of the specified element in the solid state.

The over-all rate of the processes may be affected directly or indirectly by the presence of some foreign substances.

Chemical Equilibria in Gaseous Phase: It is known that the many components of the gaseous phase stand in mutual relations like chemical equilibria although not in the strict sense of the term. Thus a metallic element may be distributed among the neutral atom, ions with positive and/or negative charge, oxide, halide, hydroxide, complex molecules and so on. Therefore, various kinds of substances, metallic and non-metallic, may possibly interact, directly or indirectly, with the specified element and consequently affect the concentration of the light-emitting species of the specified element.

Temperature: In every process mentioned above the role played by temperature is of basic importance. Hence, when the flame temperature is altered by some concomitant, nothing will remain unaltered. Rates of evaporation and the vapour pressure of each component are changed, every chemical equilibrium is altered and consequently the radiation intensity may be affected in any way.

b) Methods for Analysing the Mechanism of the Interference

The mechanism of the interference of concomitants can be classified by the process where the concomitants interfere with the specified element. "The separate atomization method" and "the location dependence method" are used to specify the process interfered with.

Separate Atomization Method: For this purpose two separate atomizers are used which work independently at the same time to spray the solution of the specified substance and the solution of the concomitant, respectively, into one and the same flame. (In the following, this method is simply called "separate atomization", whereas the ordinary method of atomization of a mixture solution of the specified substance and the concomitant with a single atomizer is called "mixture atomization".)

Two assumptions may be made for separate atomization. The first is that the specified substance and the concomitant are independent

in both liquid and solid phases, having only very rare opportunities of uniting two liquid or solid mist-particles during transport with the gas stream; and consequently the two kinds of substances are independent in the vaporization process. The second is that after entering the gaseous phase by vaporization the specified substance and the concomitant are completely mixed together and interact with each other. These two assumptions are supported by the experiments as will be shown later.

Thus interference through the process of atomization and/or vaporization may not occur with separate atomization, while the interference through the chemical equilibria in the gaseous phase and/or change of flame temperature may occur with separate atomization as well as with mixture atomization.

Therefore, when a concomitant causes some interference with the specified substance in ordinary flame excitation, the mechanism of the interference can be specified according to whether the same interference is observed with separate atomization or not. Moreover, information from the location dependence method, which will be described below, combined with separate atomization will enable more detailed analysis of the mechanism of the interferences.

Location Dependence Method: In normal flame photometry the light emitted from a fairly wide region of a flame is gathered by an optical system and admitted to a detector through an appropriate monochromator; in the present case the light from a very narrow horizontal region of a flame is picked up limitedly by a special optical device. The location where light is picked up is specified by the vertical distance, i. e., the height, from the tip-level of the inner cone of the Meker flame, and as the height is varied, the corresponding variations of an interference are analytically observed.

With increasing distance from the tip-level of the inner cone along the flow line of the gas, there must be an increasing period for a mist to be heated by the hot gases of the flame.

Moreover, with the variation of the location in a flame there may be a gradient of temperature and also somewhat complex variation in the composition of the gases.

When interference is caused by a change in the atomization process, there may be no variation of interference with the variation of the location of the measurement, because atomization processes are already over in the atomizer, and there is no correlation with the location in a flame of Meker type.

But when the interference of a concomitant is caused by a change in the rate of some processes occurring in the flame, e. g., the rate of vaporization etc., the interference may vary in a simple manner with the variation of the height of measurement. If several successive measure-

ments are made at increasing heights from the lower part to the upper part of a flame, a rate process must proceed according to the lengthened lapse of time.

The dependence of a chemical equilibrium upon the location is a little more complex, because in this case, the main factors controlling the dependence may be the temperature and the concentration of certain species in the hot gases, which are no longer simple functions of the height of the location. But the characteristics of the dependence may give useful information about the mechanism.

c) Summary of the Theory

In order to apply the above discussions to an analysis of the interference, the main points have been conveniently summarized in Table I and Table II.

Table I. Processes in flame excitation, and possible mechanisms of interference

Process	Atomization process	Rate process producing light-emitting species		Chemical equilibria in gaseous phase	Temperature
		Vaporization process	Processes in gaseous phase		
Factors possiblly influenced by concomitants	Density, viscosity, surface tension etc., of solution	Chemical and physical state in solid mist-particles; Temperature	Various	Composition of gases including vapour of solutes; Temperature	Burning conditions, heat capacity, etc.

Table II. Diagnosis of the source of interference by means of the separate atomization method and the location dependence method

Source of interference	Atomization process	Rate process producing light-emitting species		Chemical equilibria in gaseous phase	Temperature
		Vaporization process	Processes in gaseous phase		
Interference with separate atomization	No interference	No interference	?	Same interference as mixture atomization	Same interference as mixture atomization
Location dependence of interference	No dependence	Simple dependence	Simple dependence	Complex dependence	Simple dependence

Experimental

a) Apparatus

The whole arrangement of the apparatus used for these experiments is illustrated in Fig. 1.

An acetylene-air flame was used for. Acetylene gas from an ordinary iron cylinder is used with a precision pressure regulator, a needle valve and a flow meter. Room air is compressed by a compressor ($^1/_2$ HP.) to 4 atm. Water vapour and oil mists contained in the compressed air are removed by a trap cooled by ice-water and a cotton filter. Through a precision pressure regulator and a flow meter the compressed air is sent to the mixing chamber and to two atomizers, A and B. For separate atomization the solution of a specified substance and of concomitants are atomized in A and B respectively, and for ordinary mixture atomization, the mixed sample solution is atomized in A and pure water is atomized in B at the same time. The mists from both atomizers are mixed and sent to the burner from the bottom.

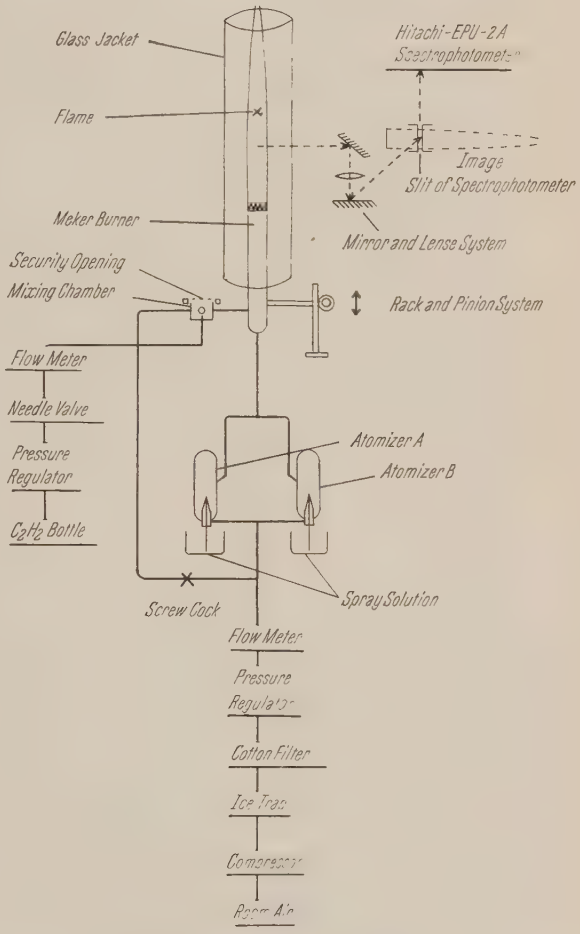

Fig. 1. Arrangement of the apparatus

A by-pass of the air supply to the mixing chamber is controlled by a screw cock to obtain an adequate acetylene to air ratio.

The burner is a specially designed Meker burner made of stainless estel. The burner tube is 15 cm long and 1.5 cm in diameter, and the

mouthpiece of 0.3 cm thick plate is drilled with 37 holes of 0.1 cm diameter. A glass cylindrical jacket of 40 cm long and 5 cm in diameter is attached around the flame area to avoid turbulence with secondary air. The position of the glass cylinder is so determined that the maximum stability of the flame may be obtained. A soft rubber tube of about 50 cm long and 1.2 cm in diameter is used to join the bottom of the burner tube with the atomizers; this rubber tube connection is effective in avoiding "singing" of the flame.

A security opening sealed with a thin polyethylene film is provided at the top of the mixing chamber and high pressure in an accidental explosion is blown off here to minimize the damage.

The whole burner unit is mounted on a stand with a rack and pinion system in order to facilitate precise vertical positioning for the choice of the location of picking up light.

The image of a flame rotated through 90° is obtained using an adequate optical system consisting of a condensor lens and two plane surface mirrors: The lens is of glass; $f = 20$ cm and diam. = 5 cm. Two plane mirrors are set in a "face to face position" in which each one is inclined 45° to the vertical axis and twisted through 90° to each other around the vertical axis. By such a system a horizontal real image (1 : 1 magnification) of a vertically long flame is obtained upon the entrance slit of the spectrometer, so that the light from a narrow limited part of the flame just fitting in the aperture of the slit is admitted into the spectrometer.

When the burner is moved vertically by the aid of the rack and pinion system, the image of the flame slips horizontally over the slit, so that the location of picking up light from the flame is changed.

The spectrometer used is the Hitachi-EPU-2 A spectrophotometer provided with a photomultiplier unit. In order to minimize rapid fluctuation of the meter needle, the valve bridge circuit has been slightly modified to increase the time constant.

b) Working Conditions

The pressure of acetyene was controlled to 0.30 kg/cm² and that of air to 4 kg/cm² at the preliminary regulator and 0.6 kg/cm² at precision regulator. The flow rates of the gases were 290 cm³/sec for air and 27.6 cm³/sec for acetylene measured at 1 atm. and 15° C.

With these conditions a very stable laminar flame with a visible part of about 50 cm high and about 1.5 cm in diameter was obtained. The inner cones were about 0.5 cm high.

Measurements were made of the 423 nm (1 nm = 10^{-9} m) atomic line and the 622 nm band-head of calcium with 0.2 — 0.4 mm slit openings and also of the 780 nm line of rubidium with 0.15 mm slit opening.

The zero point was usually adjusted so that the "background" gave zero reading on meter scale.

Results were adopted only when two successive readings agreed within a range of 1%. The intermittent feed of water was seemed to disturb the thermal equilibria and burning conditions: In order to obtain reproducible readings, the next solution is fed from atomizer as soon as one sample is removed.

c) Reagents and Preparation of Sample

All the reagents employed were "special grade" of JIS (Japan Industrial Standard).

For the preparation of the standard stock solutions of H_3BO_3, KCl, RbCl, a definite amount of each substance was accurately weighed and made up in distilled water to a definite volume.

For $CaCl_2$ solution, an adequate amount of $CaCO_3$ was dissolved in the minimal quantity of hydrochloric acid and distilled water was added to an adequate volume. For $Al(NO_3)_3$, $NH_4H_2PO_4$, $(NH_4)_2SO_4$, the concentration of each stock solution is determined by gravimetric analyses.

The calculated volumes, not less than 2 ml of stock solutions, were taken from the burette into a 100 ml measuring flask and pure water was added to the mark.

Results and Discussions

a) Comparisons Between Mixture Atomization and Separate Atomization

Comparisons were made between ordinary mixture atomization and separate atomization, for cases where calcium chloride was the specified substance and aluminium, borate, phosphate and sulphate were concomitants, respectively. The concentration of calcium chloride was chosen to be 5.0 meq/l. (Here, 1 eq. is the amount of a specified substance containing 1 gram atom of the specified element[2].)

Results are shown in Fig. 2–9. For each case measurements were made with the 423 nm atomic line and the 622 nm band head. (Recently this band has been assigned to the $Ca(OH)_2$ molecule[13].) In those figures, black lines indicate the results of mixture atomization, where the intensities were measured when mixed solutions containing 5.0 meq/l $CaCl_2$ and a concomitant at various concentrations were sprayed from atomizer A. Broken lines indicate the results of separate atomization, where the intensities were measured when 5.0 meq/l $CaCl_2$ solution and the solution of the concomitant of various concentrations were separately sprayed from atomizer A and B, respectively.

In every figure the % intensity is taken as ordinate and 100% is set to be the intensities when there is no interference of concomitant; the concen-

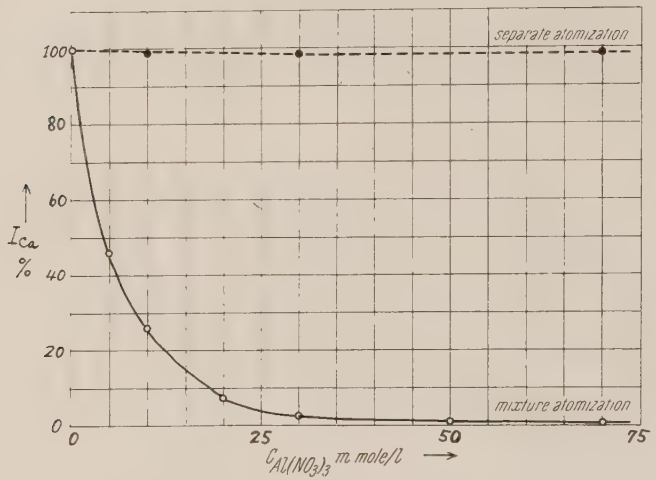

Fig. 2. Interference of Al with the Ca 423 nm line; comparison between mixture atomization and separate atomization (Ca: 5.0 meq/l)

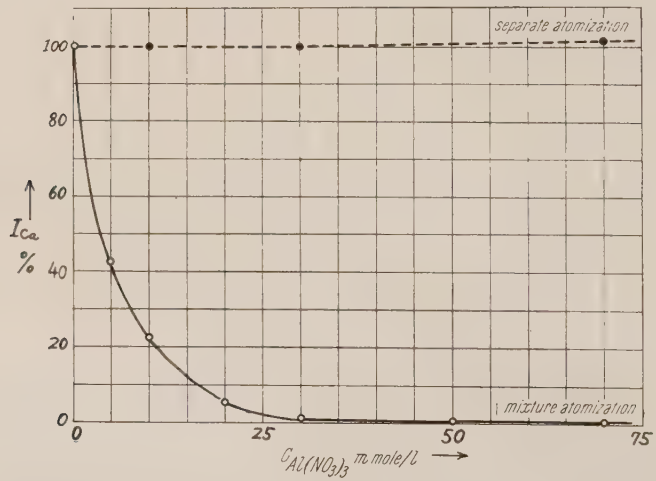

Fig. 3. Interference of Al with the Ca 622 nm band; comparison between mixture atomization and separate atomization (Ca: 5.0 meq/l)

tration of concomitant is expressed in m mole/l unit and taken as abscissa.

Atomizers A and B were shown to be identically efficient, because the results were almost the same if the two atomizers were used inter-

changeably. Therefore the rates of feed of the concomitant into the flame are presumed to be identical whether the concomitant is sprayed

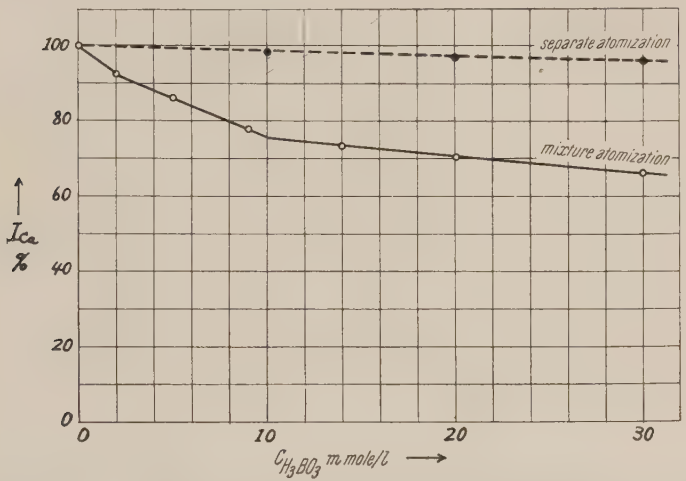

Fig. 4. Interference of BO_3^{3-} with the Ca 423 nm line; comparison between mixture atomization and separate atomization (Ca: 5.0 meq/l)

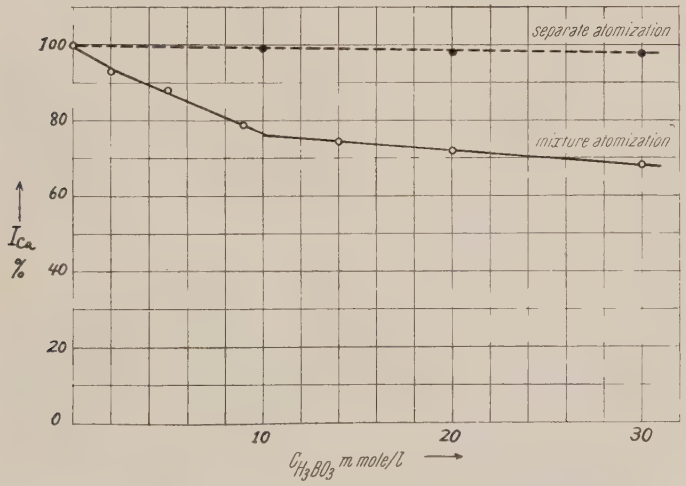

Fig. 5. Interference of BO_3^{3-} with the Ca 622 nm band; comparison between mixture atomization and separate atomization (Ca: 5.0 meq/l)

by atomizer A (in case of mixture atomization) or by atomizer B (in case of separate atomization), so long as the concentrations of the concomitant in the spray solutions are the same.

It should be remarked here that in order to avoid confusion in these figures the results are shown only for cases where measurements were done at 1 mm above the tip-level of the inner cones. When measurements were done at other heights, the separate atomization method always gave the same results, whereas the mixture atomization method gave different ones. This is very significant and the results will be shown in the next section ("location dependence of interference") in detail.

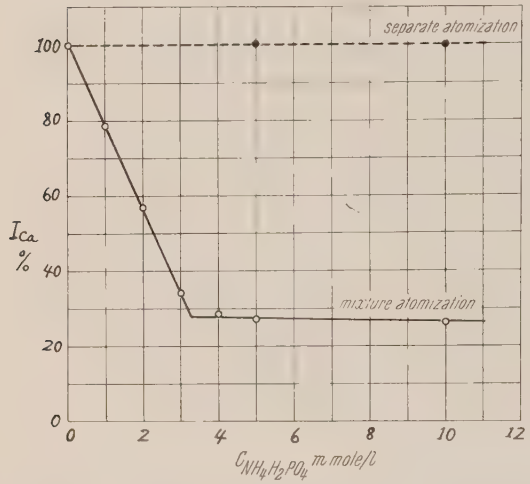

Fig. 6. Interference of PO_4^{3-} with the Ca 423 nm line; comparison between mixture atomization and separate atomization (Ca: 5.0 meq/l)

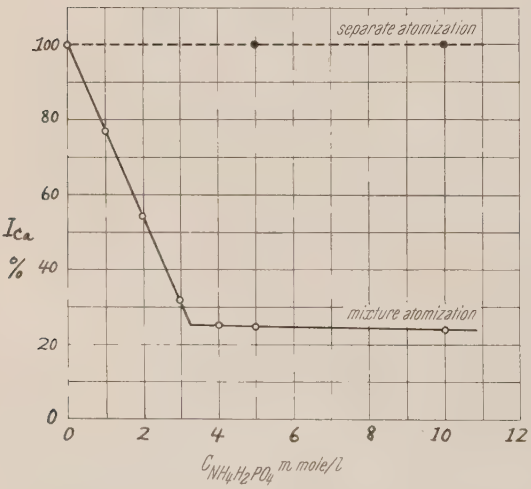

Fig. 7. Interference of PO_4^{3-} with the Ca 622 nm band; comparison between mixture atomization and separate atomization (Ca: 5.0 meq/l)

In all cases given in these figures the results have shown a profound difference between mixture atomization and separate atomization. That is, the marked suppressing effects of aluminium, borate, phosphate and sulphate upon the calcium radiation are almost completely absent when calcium and those extraneous substances are introduced from separate atomizers into the flame.

Here should be recollected the prerequisite assumptions of separate atomization, that the specified substance and the concomitant are independent in the liquid and solid phases, because the chances of uniting two liquid or solid mist particles are very rare, and that the two kinds of substances, after entering into gaseous phase, are completely mixed together and have interactions with each other.

The second of these assumptions may be doubted, because all the cases of the experiments with separate atomization did not show the interfering phenomena.

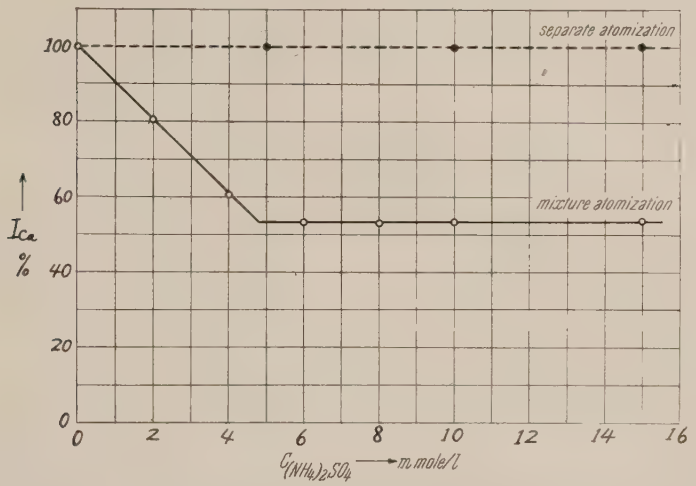

Fig. 8. Interference of SO_4^{2-} with the Ca 423 nm line; comparison between mixture atomization and separate atomization (Ca: 5.0 meq/l)

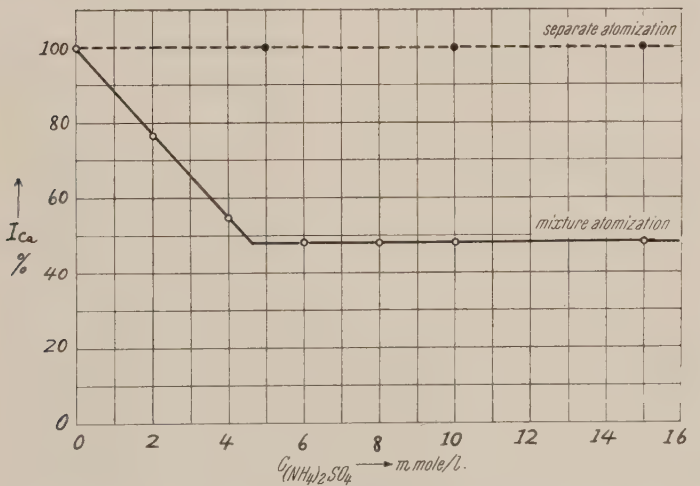

Fig. 9. Interference of SO_4^{2-} with the Ca 622 nm band; comparison between mixture atomization and separate atomization (Ca: 5.0 meq/l)

The next experiment was done in order to answer the doubt whether the specified substance and the concomitant, separately introduced into flame, are really mixed sufficiently to be able to interact with each other in gaseous phase.

For this purpose the interference of potassium with rubidium radiation was tested, because those alkalies have been believed to interact with each other through ionization equilibrium[1] in the flame, and separate atomization should give the same effect as mixture atomization. If separate atomization showed no interference, the validity of the separate atomization method might be doubted.

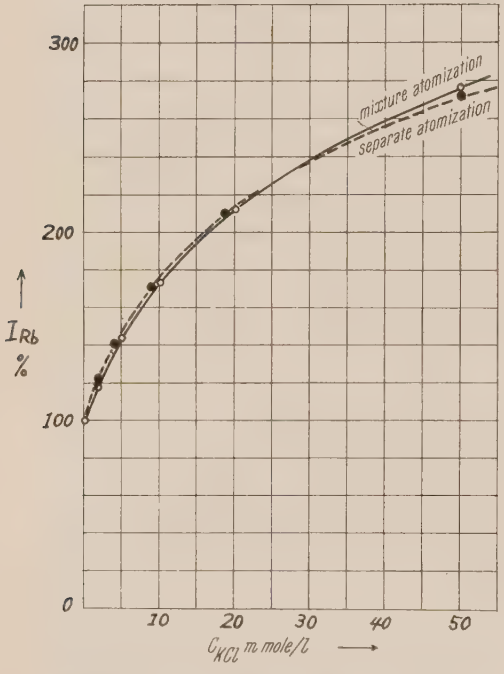

Fig. 10. Interference of K with the Rb 780 nm line; comparison between mixture atomization and separate atomization (Rb: 5.0 meq/l)

The results obtained at a height of 20 mm above the tip-level of inner corns are given in Fig. 10 as an example, where the intensity of the 780 nm line of rubidium was greatly increased by potassium (the additive interference occured was subtracted adequately) in mixture atomization and also in separate atomization. The results at other heights were similar.

From these results one conclusion is that the two assumptions of the separate atomization method are really valid, i. e., the specified substance and the concomitant are independent before entering the gaseous phase and are adequately mixed to interact with each other in the gaseous phase.

From the fact that in separate atomization, aluminium, borate, phosphate and sulphate do not show the main feature of the suppressing effect on the calcium radiation, it can be definitely concluded that the suppressing effect is due to neither the change in the flame temperature nor the shift of chemical equilibrium, but that either some hindrance of the atomization process and/or some rate process producing light-emitting species (including a vaporization process) must be responsible for the effect.

b) Location Dependence of the Interferences

With mixture atomization, measurements were done at various heights (1–150 mm) above the tip-level of the inner cones. Here again

the specified substance was calcium chloride (5.0 meq/l) and aluminium, borate, phosphate, and sulphate were concomitants. For each case

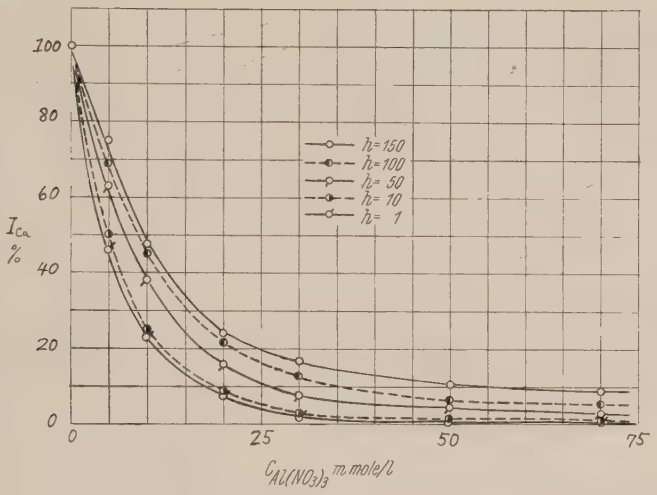

Fig. 11. Location dependence of the interference of Al with the Ca 423 nm line, mixture atomization; h = height from the tip-level of inner cones in mm

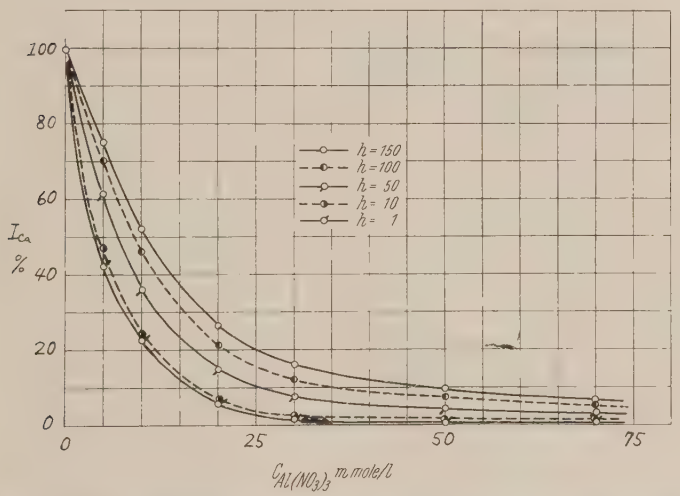

Fig. 12. Location dependence of the interference of Al with the Ca 622 nm band, mixture atomization; h = height from the tip-level of inner cones in mm

measurements were made at both 423 nm and 622 nm. The results are shown in Fig. 11–18.

The % intensity is taken as ordinate and at every height the intensities are so standardized to read 100% when the pure solution of 5.0 meq/l $CaCl_2$ containing no concomitant is fed into the flame. The abscissae are the concentrations of concomitants in the mixture solution.

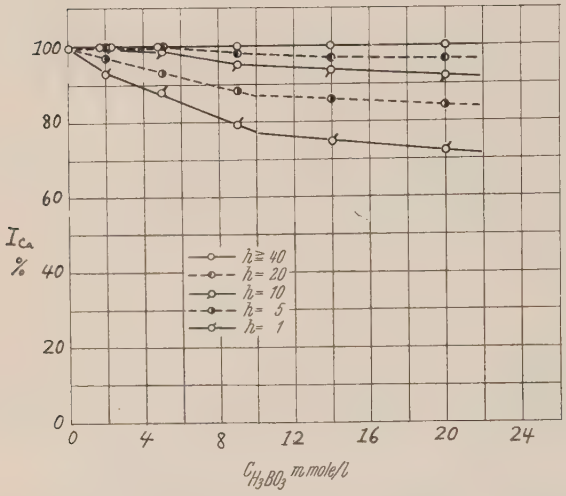

Fig. 13. Location dependence of the interference of BO_3^{3-} with the Ca 423 nm line, mixture atomization; h = height from the tip-level of inner cones in mm

The heights where measurements were done are expressed by vertical distance from the level of tips of the inner cones and given in each figure.

It is remarkable that the suppressing effects of aluminium, borate, phosphate, and sulphate become the less, the higher the location of the measurements. The "recoveries" of calcium radiation suppressed by various concomitant can be seen explicitly in Fig. 19 to 22. In these figures a certain representative concentration for each one of the concomitants is chosen, and the same results as those plotted in Fig. 11–18 are reproduced, but the heights from tip-level are taken as abscissae.

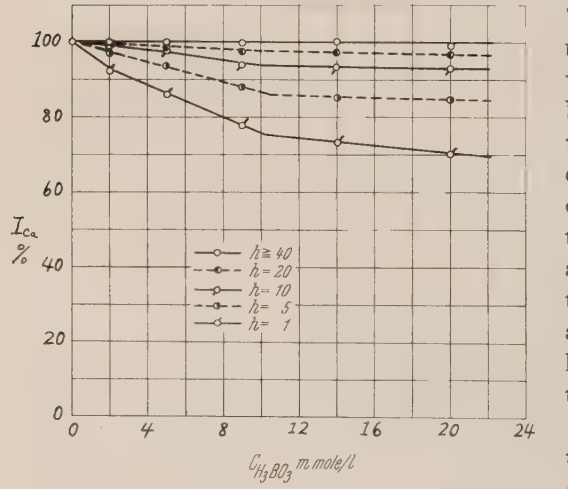

Fig. 14. Location dependence of the interference of BO_3^{3-} with the Ca 622 nm band, mixture atomization; h = height from the tip-level of inner cones in mm

It is noteworthy that the data of the 423 nm atomic line and of the 622 nm band head agree with each other within experimental error.

The suppression of calcium radiation by aluminium (Fig. 11, 12, 19) is decreased gradually as the height of observation is raised, but the

recovery of the radiation is less than 10% when a large quantity of aluminium is present. In contrast, the suppressions by borate (Fig. 13, 14, 20) and by sulphate (Fig. 17, 18, 22) diminish rather rapidly and at higher than several cm (ca. 4 cm in the case of borate, ca. 8 cm in the case of sulphate, respectively) from the tip-level of the inner cones, the suppressing effects can be no longer seen. In the case of phosphate (Fig. 15, 16, 21) the situation is somewhat intermediate, that is, the calcium radiation suppressed by phosphate is recovered very gradually but almost completely. But when the concentration of phosphate is very large, the recovered intensity is no more than 98% even at 150 mm high from the tip-level.

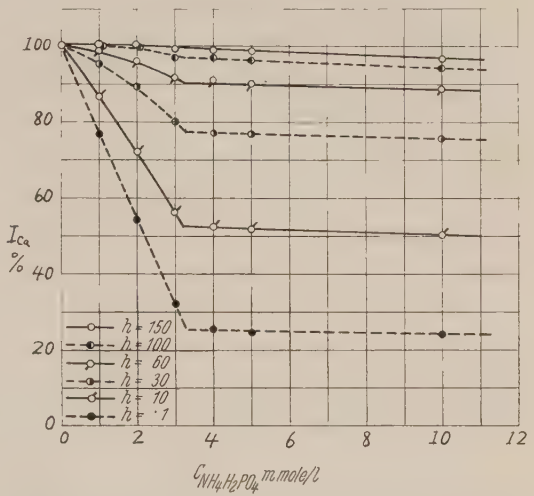

Fig. 15. Location dependence of the interference of PO_4^{3-} with the Ca 423 nm line, mixture atomization; h = height from the tip-level of inner cones in mm

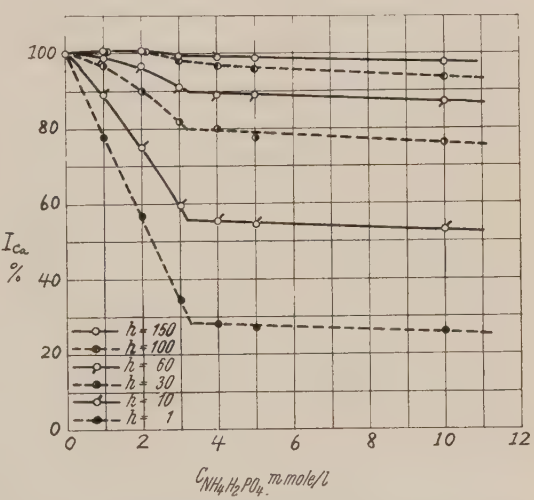

Fig. 16. Location dependence of the interference of PO_4^{3-} with the Ca 622 nm band, mixture atomization; h = height from the tip-level of inner cones in mm

c) Conclusions

Mechanism of Interferences: Here should be recollected the important conclusion of the separate atomization method that the suppressing effects of these substances are either due to a hindrance in atomization process and/or some rate process producing light-emitting species.

Then the general tendency that the radiation of calcium suppressed by aluminium, borate, phosphate, and sulphate is recovered markedly

at measurable rates, as the height from the tip-level is increased, is very suggestive.

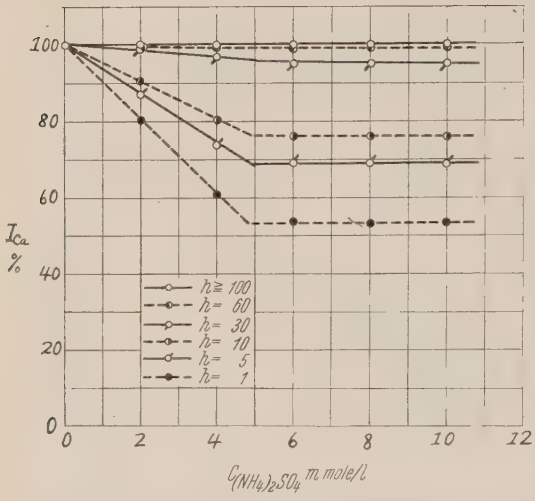

Fig. 17. Location dependence of the interference of SO_4^{2-} with the Ca 423 nm line, mixture atomization; h = height from the tip-level of inner cones in mm

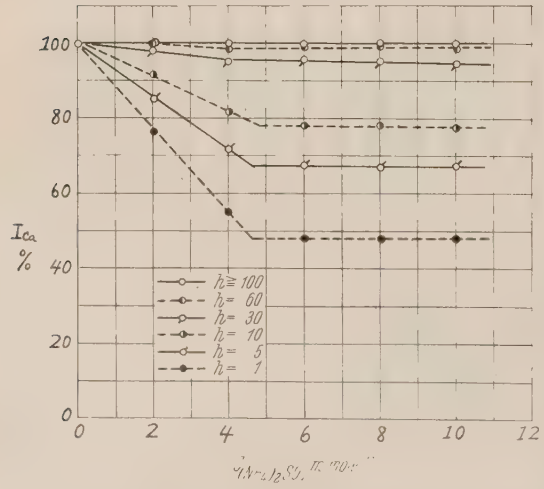

Fig. 18. Location dependence of the interference of SO_4^{2-} with the Ca 622 nm band, mixture atomization; h = height from the tip-level of inner cones in mm

These experimental facts obtained by both separate atomization and location dependence methods, as has been discussed in the theoretical section, can be most easily interpreted by assuming that the suppression of calcium radiation by aluminium, borate, phosphate and sulphate is caused by hindering rate processes producing the light-emitting species of calcium.

Of these rate processes, one occurring in the gaseous phase seems less probable, because no spectral indication has been observed of the occurrence of any special compound in the flame gases when mixed solutions of calcium and the interfering substances are introduced into the flame. The more probable conclusion is that the suppressing effects of these substances are mainly due to reduction of the vaporization rate of calcium from a condensed phase to a gaseous state. This conclusion seems consistent with the fact that all the experimental results are completely the same for both the 423 nm atomic line and the 622 nm hydroxide band head.

However, more experiments may be necessary in order to interpret the detailed features of the interference, e. g., that the separate atomization with aluminium and borate shows a slight interference (Fig. 2–5) and

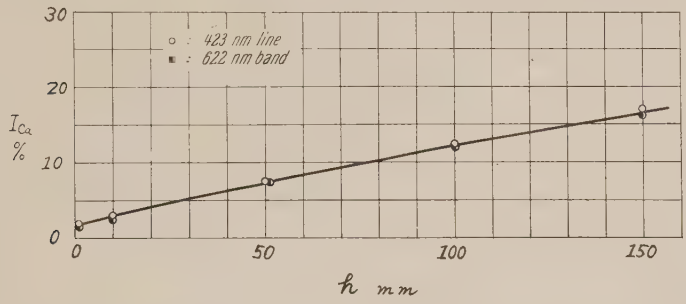

Fig. 19. Recovery of Ca radiation suppressed by Al (Ca = 5.0 meq/l, $Al(NO_3)_3$ = 30 mmol/l)

that the recovery of calcium radiation suppressed by phosphate is not really complete (Fig. 15, 16, 21) when the concentration of the phosphate is relatively high.

The reason why the rate of vaporization of calcium is reduced by the addition of aluminium, borate, phosphate and sulphate should next be considered. As has been pointed out somewhat ambiguously by some authors, the formation of a non-volatile compound seems most reasonable, because in Fig. 13–18 the precise stoichiometric relations between calcium and each of borate, phosphate and sulphate are very clearly seen. There is no information about the formulae of the compounds but the composition may correspond to the atomic ratios of the breaks in the curves in these figures, namely, Ca/B = 1/2, Ca/P = 3/2, Ca/S = 1/1.

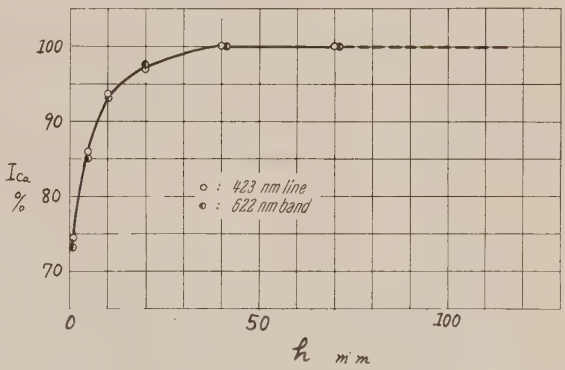

Fig. 20. Recovery of Ca radiation suppressed by BO_3^{3-} (Ca = 5.0 meq/l, H_3BO_3 = 14 mmol/l)

In the case of aluminium such a similar definite stoichiometric relation cannot be observed; although it is not certain, the formation of a non-volatile compound which should be of uncertain composition might be suspected by analogy.

Concerning the effects of phosphate, in 1954 *Dippel* et al.[14] reported that phosphoric acid at very high concentration gave a marked enhancement of the radiations of calcium and magnesium. This, if true, must be

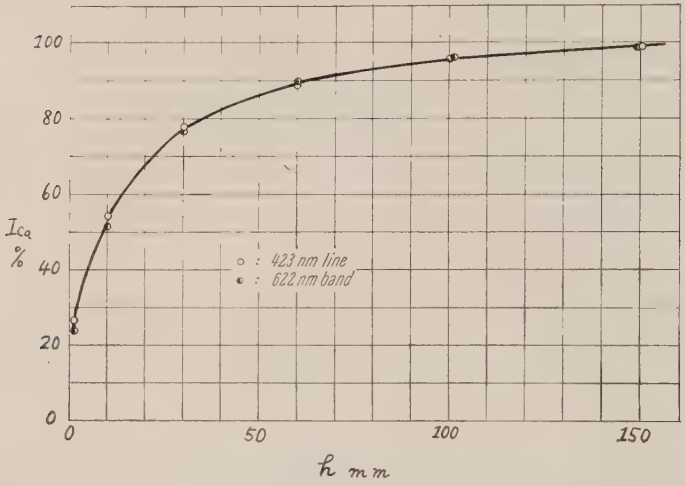

Fig. 21. Recovery of Ca radiation suppressed by PO_4^{3-} (Ca = 5.0 meq/l, $NH_4H_2PO_4$ = 5.0 mmol/l)

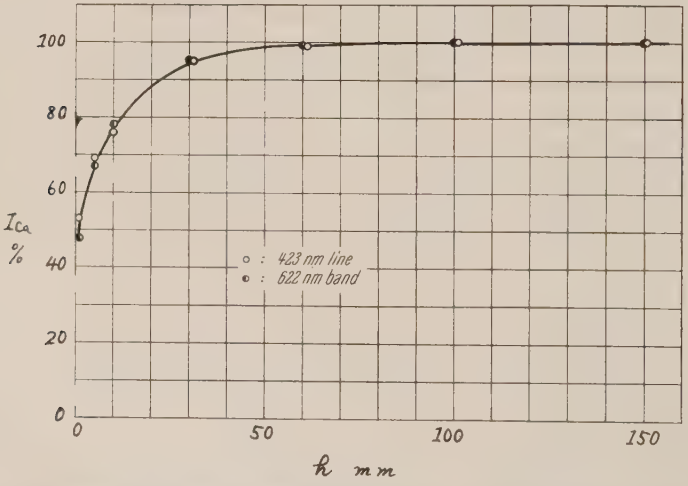

Fig. 22. Recovery of Ca radiation suppressed by SO_4^{2-} (Ca = 5.0 meq/l, $(NH_4)_2SO_4$ = 6.0 mmol/l)

a serious argument against the mechanism deduced above. I have therefore made very elaborate tests of their result. But their finding could not be confirmed, and when the strong radiation from phosphoric

acid itself was accurately subtracted, there was no net enhancement, but only ordinary suppression of the radiations of the alkaline earths. Therefore, I believe that phosphate even at very high concentration only has a suppressing effect on the calcium radiation together with a very remarkable additive interference.

Elimination of Interferences: From the view point of practical analysis, the results of the location dependence method appear to be very interesting, because the wellknown interferences of borate, phosphate and sulphate are no longer found at the higher parts of the flame with the special burner described. This suggests a new design of flame photometers which should give freedom from the troublesome interferences of these substances with the alkaline earths. An investigation along this line is being carried out.

Separate Atomization and Location Dependence Methods: It has been exemplified by the above experiments that the separate atomization method and the location dependence method can be very powerful tools for investigating the mechanism of an interference in flame photometry. When the mechanism of an interference is understood, its elimination can be successfully achieved.

Acknowledgement

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Summary

The mechanism of the suppressing effects of aluminium, borate, phosphate, sulphate upon calcium radiation has been investigated. A very stable long flame was used with a specially designed Meker Burner. Variations in the interferences were observed when Ca and those interfering substances were separately atomized into one and same flame, and also when the point in the flame from which the light was drawn was changed by the use of a specially designed optical system attached to a Hitachi-EPU-2 A spectrophotometer. It is concluded that the suppression of Ca radiation is caused by hindering of the vaporization process because of the formation of non-volatile compounds of Ca with those interfering substances.

A method of eliminating the suppressing effects of borate, phosphate and sulphate on alkaline earth radiations has been suggested.

Zusammenfassung

Die durch Aluminium, Borat, Phosphat und Sulfat hervorgerufene Intensitätsminderung der durch Calcium bedingten Flammenfärbung wurde untersucht. Ein besonders konstruierter Meker-Brenner wurde zur Erzeugung einer sehr konstanten und langen Flamme verwendet. Versprüht man das Calcium und die erwähnten Störstoffe in dieselbe Flamme oder wechselt man die zur Lichtmessung gewählte Flammenregion unter Verwendung eines dafür geeigneten, an einem Hitachi-EPU-2 A-Spektrophotometer angebrachten optischen Systems, so zeigen sich jeweils verschieden starke Störungen. Daraus ergibt sich, daß die Unterdrückung der Calcium-Strahlung durch eine Beeinträchtigung des Verdampfungsvorganges infolge Bildung nichtflüchtiger Verbindungen verursacht wird, die sich aus Calcium und den angeführten Störstoffen bilden.

Ein Verfahren zur Beseitigung des durch Borat, Phosphat und Sulfat herbeigeführten Unterdrückungseffektes auf alkalische Erden wurde vorgeschlagen.

Résumé

Recherche sur le mécanisme des effets de suppression de l'aluminium, des borates, des phosphates, des sulfates sur la radiation du calcium. A cette fin, l'auteur a employé une flamme longue, très stable d'un brûleur Meker spécialement prévu. Des variations de ces effets ont pu être constatées lorsque le calcium et les substances gênantes étaient atomisés séparément dans un flamme unique et lorsqu'on faisait varier le point de la flamme émetteur de la lumière observée; ces mesures ont été rendues possibles par l'emploi d'un système optique spécialement conçu fixé à un spectrophotomètre Hitachi-EPU-2 A. La conclusion de ce travail est que la suppression de la radiation du calcium est dûe à un processus d'empêchement de la vaporisation inhérent à la formation de composés non volatils du calcium avec les substances gênantes.

L'auteur suggère une méthode permettant l'élimination des effets de suppression des borates, des phosphates et des sulfates sur les radiations des alcalino-terreux.

Literature

[1] *E. Pungor, A. J. Hegedüs, I. K. Thege,* and *E. É. Zapp,* Mikrochim. Acta [Wien] **1956**, 1247.

[2] *S. Fukushima, M. Shigemoto, I. Kato,* and *K. Otozai,* Mikrochim. Acta [Wien] **1957**, 35.

[3] *C. D. Child,* Phys. Mag. **16**, 1141 (1933).

[4] *R. L. Mitchell* and *I. M. Robertson,* J. Soc. Chem. Ind. **55**, 269 (1936).

[5] *L. Huldt,* Arkiv Matematik, Astronomi, Fysik **33 A**, No. 5 (1946).

[6] *T. Török,* Z. analyt. Chem. **119**, 120 (1940).

[7] *J. Köhnlein* and *K. E. Lücke,* Bodenkund. Pflanzenernähr. **57**, 114 (1952).

[8] *L. Leyton,* Analyst **79**, 497 (1954).

[9] *S. Ikeda,* Nihon Kagaku Zasshi (J. Japan Chem. Soc., in japanese) **78**, 1431 (1957).

[10] *S. Tsuchihashi* and *E. Sekido,* Nihon Kagaku Zasshi (J. Japan Chem. Soc., in japanese) **77**, 708 (1956).

[11] *M. Margoshes* and *B. L. Vallee,* Analyt. Chemistry **28**, 180 (1956).

[12] *G. L. Baker* and *L. H. Johnson,* Analyt. Chemistry **26**, 465 (1954).

[13] *C. G. James* and *T. M. Sugden,* Nature **175**, 334 (1955).

[14] *W. A. Dippel, C. E. Bricker,* and *N. H. Furman,* Analyt. Chemistry **26**, 553 (1954).

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Zur Bestimmung der Mutterkornalkaloide mit p-Dimethylaminobenzaldehyd

Von

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Als Reagens für die photometrische Bestimmung der Mutterkornalkaloide wird im allgemeinen p-Dimethylaminobenzaldehyd in schwefelsaurer Lösung unter Zusatz einer geringen Menge einer Eisen(III)-chloridlösung verwendet. Nach Zugabe von zwei Teilen des Reagens zu einem Teil einer weinsauren Alkaloidlösung entsteht hierbei eine Blaufärbung. Diese Farbreaktion war bereits mehrmals Gegenstand eingehender Untersuchungen. Trotzdem erscheint eine erneute Überprüfung gerechtfertigt, da widersprechende Angaben vorliegen.

Die Reaktion wurde zunächst von *H. W. van Urk*[1] beschrieben und von *M. I. Smith*[2] verbessert. Dieser wie auch *N. L. Allport* und *T. T. Cocking*[3] fassen sie als einen photochemischen Vorgang auf. *Allport* und *Cocking* schreiben dem von ihnen empfohlenen Zusatz von Eisenchlorid, der eine starke Belichtung der Reaktionslösung nicht mehr notwendig macht, nur katalytische Wirkung zu. Die genannten Autoren geben weiterhin an, daß Oxydations- und Reduktionsmittel den Ablauf der Reaktion empfindlich stören. Dagegen weisen *E. Schulek* und *G. Vastagh*[4] auf den im wesentlichen chemischen Charakter der Reaktion hin, wobei $FeCl_3$ als Oxydationsmittel anzusehen sei*, während nach Angaben von *I. Molnár* und *H. Uskert*[5] die Farbreaktion nur in Gegenwart von wenig Manganionen quantitativ verläuft. Der Träger dieser Farbreaktion ist nach *P. Tuzson*, *J. Tuzson* und *J. Bayer*[6,7] der Lysergsäureanteil des Moleküls. Daher werden sämtliche Alkaloide der Lysergsäure- bzw. der Isolysergsäurereihe, wie auch hydrierte Alkaloide, Lichtalkaloide, partial-synthetische Derivate und die Clavine gleichermaßen

* Sie schlagen jedoch eine Variation des Reagens mit H_2O_2 als Oxydans vor, wobei dessen Überschuß nach 2 Minuten mit $NaHSO_3$ zu beseitigen ist. Dieses Verfahren hat sich nicht durchgesetzt, da in allen zur Zeit berücksichtigten Arbeitsvorschriften fast ausschließlich Reagenslösungen mit alleinigem $FeCl_3$-Zusatz Anwendung finden.

erfaßt. Nach *M. Pöhm*[8] erfolgt hierbei eine Wasserabspaltung zwischen zwei Molekülen Lysergsäure und einem Molekül Aldehyd und bei anschließender Oxydation durch Eisen(III)-chlorid Bildung eines Farbsalzes vom Typus des Rosindols.

A. Silber und *T. Schulze*[9] berichten jedoch, daß mit diesem Reagens trotz des Eisenchloridzusatzes, der nach ihren Angaben katalytisch wirkt, selbst innerhalb 1 Stunde keine maximale Farbentwicklung eintritt und daß eine UV-Bestrahlung notwendig ist. Da andererseits ohne Eisenchloridzusatz eine UV-Bestrahlung unzureichend ist, müssen nach Angaben von *Silber* und *Schulze* beide Faktoren, Eisenchloridzusatz und UV-Bestrahlung gekoppelt sein, um eine maximale Farbintensität sicherzustellen. Während bei Reinalkaloiden eine 20 Minuten lange UV-Belichtung angegeben wird — eine längere UV-Einwirkung führt zur Abnahme der Extinktion —, ist bei Extraktionslösungen aus Mutterkorn nur eine Bestrahlungszeit von 5 bis 7 Minuten mit einer Hg-Dampflampe zur Erreichung des Extinktionsmaximums vorgesehen. Dieses Arbeitsverfahren wurde in der Folgezeit von anderen Autoren übernommen[10]. In einem Vorschlag zum Nachtrag des DAB 6 sieht auch *K. H. Renneberg*[11] zur Intensivierung der Blaufärbung beim qualitativen Nachweis der Alkaloide eine UV-Bestrahlung vor.

In der Papierchromatographie wird nach *J. Tuzson* und *G. Vastagh*[7] wie auch nach *J. Kolšek*[12] gleichfalls eine Steigerung der Farbintensität der mit p-Dimethylaminobenzaldehyd-Reagens angefärbten Alkaloide durch UV-Bestrahlung erreicht. Ebenso lassen sich nach *H. Rochelmeyer, E. Stahl* und *A. Patani*[13] hiermit Dihydroalkaloide in stark gelbgrün-fluoreszierende Verbindungen umwandeln, wodurch diese Alkaloide nunmehr leicht auf dem Chromatogramm zu erkennen sind.

Bei eigenen Versuchen ließen sich die mit dem von uns benutzten Reagens* nach 20 bis 30 Minuten photometrisch** erhaltenen Werte weder durch Verlängerung der Wartezeit, noch durch zusätzliche UV-Bestrahlung*** erhöhen. Im Gegenteil machte sich im letzteren Fall bereits ein Abfall der Blauwerte bemerkbar. Bei vergleichenden Untersuchungen mit einem nach *Silber* und *Schulze* hergestellten Reagens†, das gewisse quantitative Unterschiede gegenüber dem unserigen aufweist, ließen sich die von den Autoren gemachten Angaben weitgehend bestätigen.

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* Zu einer Mischung von 35 ml Wasser und 65 ml konz. Schwefelsäure werden 0,2 g p-Dimethylaminobenzaldehyd und 0,03 ml Eisen(III)-chloridlösung DAB 6 (= 10% Eisen) hinzugefügt (vgl. *L. Fuchs*[14]).

** Die Messungen erfolgten mit dem Pulfrich-Stufenphotometer.

*** Zur Bestrahlung wurde das Gerät „Elmed-Lumina-U" der Fa. Elmed, Hohen Neuendorf b. Berlin, benutzt. Das Reaktionsgemisch befand sich in Kristallisierschalen, Durchmesser 3 cm, die einen Abstand von etwa 27 cm vom Quecksilberbogen hatten. Ein Filter wurde nicht eingeschaltet.

† 0,2 g p-Dimethylaminobenzaldehyd gelöst in 100 ml 65%iger Schwefelsäure + 0,03 ml 10%ige Eisen(III)-chloridlösung. Da *Silber* und *Schulze* demnach keine Angaben über den Gehalt der Eisenchloridlösung machten, wurde zu deren Herstellung $FeCl_3 \cdot 6\,H_2O$ (10,0 g/100 ml) verwendet. Eine derartige Lösung enthält zirka 2% Eisen.

Auch eine Gegenüberstellung des in den Arzneibüchern und in der Literatur aufgeführten p-Dimethylaminobenzaldehyd-Reagens läßt erkennen, daß zwar die qualitative Zusammensetzung der einzelnen Reagenslösungen übereinstimmt, die Aldehydmenge sowie der Eisenchloridzusatz jedoch wie auch die Konzentration der Schwefelsäure in gewissen Grenzen variieren. Im allgemeinen werden 0,12 bis 0,25% Aldehyd in 50- bis 75%iger Schwefelsäure gelöst. Recht unterschiedlicher Natur sind die Angaben über den Eisen(III)-chloridzusatz. Abgesehen von einigen papierchromatographischen Arbeiten, in denen auf das van Urksche Reagens verwiesen, also auf jegliche Zugabe verzichtet wird, sieht die Britische Pharmakopoe 1953 0,1 ml einer 5%igen Eisen(III)-chloridlösung vor*, die aus kristallwasserfreiem $FeCl_3$ herzustellen ist. 0,1 ml einer 5%igen Eisenchloridlösung ist die angegebene Menge des Zusatzes nach der Pharmakopoe der UdSSR VIII (1952). Dieses Arzneibuch versteht unter Eisenchlorid das Salz der Formel $FeCl_3 \cdot 6\,H_2O$. Die Internationale Pharmakopoe (Editio Prima) läßt 0,1 ml einer 4,5%igen Eisenchloridlösung hinzufügen, die aus $FeCl_3 \cdot 6\,H_2O$ bereitet wird, während die U. S. Pharmakopoe 1953 0,05 ml einer Lösung vorschreibt, die 9% $FeCl_3 \cdot 6\,H_2O$ enthält. 0,1 ml einer 0,1-m Eisenchloridlösung sind nach der Dänischen Pharmakopoe IX vorgeschrieben. 0,03 ml der offizinellen Eisenchloridlösung (10% Eisen) werden von *L. Fuchs* und *W. Himmelbauer*[14] wie auch von *L. Fuchs*, *M. Hecht* und *M. Pöhm*[15] vorgesehen. Liqu. ferri sesquichlorati benutzt auch *G. Schumacher*[16], wobei er einen Normaltropfen auf 100 ml Reagens empfiehlt. *I. Corubolo* und *M. Grims*[17] arbeiten mit einer 5%igen Eisen(III)-chloridlösung (0,1 ml). Zwei Tropfen einer gleichprozentigen Eisenlösung enthält das von *R. Fischer* und *M. Hecht*[18] verwendete Reagens. *A. Silber* und *T. Schulze*[9] geben als Zusatz 0,03 ml einer 10%igen Eisen(III)-chloridlösung an und *E. Thielmann*, *W. Lang* und *H. Kaiser*[19] lösen 0,1 g $FeCl_3 \cdot 6\,H_2O$ direkt in ihrem Reagens auf.

Diese Aufzählung der unterschiedlichen Zusammensetzungen ist nicht erschöpfend.

Die mit den beiden beschriebenen Reagenslösungen erzielten, nicht übereinstimmenden Werte wurden zunächst dem unterschiedlichen Eisenchloridgehalt zugeschrieben. Das würde bedeuten, daß Eisenchlorid nicht katalytisch, sondern zumindest vornehmlich als Oxydationsmittel fungiert und somit für einen quantitativen Verlauf der Reaktion ausreichende Mengen dieses Stoffes zur Verfügung stehen müssen. Dies sollte durch folgende Versuchsanordnung überprüft werden.

1 ml einer weinsauren Ergotaminlösung wurde mit 2 ml eines p-Dimethylaminobenzaldehydreagens (0,2% Aldehyd in 75%iger Schwefelsäure) versetzt, das in einem Fall keinerlei Eisenchloridzusatz enthielt, während den anderen Proben steigende Mengen Eisenchloridlösung zugefügt wurden. In der Tabelle 1 werden die Milliliter einer Eisenchloridlösung (10 g $FeCl_3 \cdot 6\,H_2O$/100 ml) angeführt, die jeweils 10 ml des Reagens zugesetzt waren.

* Bezogen jeweils auf 100 ml Reagens.

Tabelle 1. Einfluß des Eisenchloridzusatzes zum Reagens auf den quantitativen Verlauf der Reaktion

Ergotamin zirka 200 μg/ml; Filter S 61; 0,5 cm Schichtdicke

ml der $FeCl_3$-Lösung	1. 0,00	2. 0,005	3. 0,01	4. 0,03	5. 0.05	6. 0,08	7. 0,10	8. 0,20	9. 0,30
	Extinktionen								
30 Minuten Wartezeit (Tageslicht)	0,19	0,76	0,84	0,85	0,85	0,82	0,79	0,70	0,63
Anschließend 10 Minuten UV-Bestrahlung	0,64	0,80	0,84	0,85	0,84	0,81	0,78	0,69	0,62

Während die Reagenslösungen 1 bis 5 nahezu farblos waren, zeigten die Lösungen 6 bis 9 infolge des hohen Eisenchloridzusatzes eine leicht gelbliche Verfärbung. Die Versuche ergaben (Tabelle 1), daß selbst bei UV-Bestrahlung mit dem Reagens ohne Eisen(III)-chlorid keine maximale Extinktion zu erreichen war, daß jedoch ein bestimmter Zusatz der Eisenchloridlösung ausreichte, um die Farbreaktion quantitativ zu gestalten. Bei einer beträchtlichen Erhöhung des $FeCl_3$-Zusatzes verringerten sich infolge Zerstörung des Farbstoffes die Extinktionswerte. Zur weiteren eingehenden Klärung des Einflusses des Eisen(III)-chlorids wurden an drei Alkaloidlösungen (zwei stärkeren und einer schwächeren) steigende Eisensalzmengen enthaltende Reagenslösungen überprüft. Zu deren Herstellung wurden jeweils 0,2 g p-Dimethylaminobenzaldehyd in einer Mischung aus 65 ml konz. Schwefelsäure und 35 ml H_2O gelöst, dann die nachstehend angegebene Menge einer $FeCl_3$-Lösung (10 g $FeCl_3 \cdot 6\ H_2O$/100 ml) zugefügt (= Reagenslösungen A).

Reagenslösung A/1 = 0,00 ml Eisenchloridlösung
„ A/2 = 0,01 ml „
„ A/3 = 0,02 ml „
„ A/4 = 0,03 ml „
„ A/5 = 0,05 ml „
„ A/6 = 0,10 ml „
„ A/7 = 0,15 ml „
„ A/8 = 0,20 ml „

Die Tabelle 2 enthält die ermittelten Werte.

Die Übersicht zeigt ein Ansteigen der Extinktionen mit der Zunahme des Eisenchloridgehaltes. 0,15 ml einer 10%igen Eisenchloridlösung waren in allen Fällen (meist schon 0,1 ml) ausreichend, um das Extinktionsmaximum zu erreichen. Eine höhere Eisenchloridmenge blieb ohne Einfluß auf die Meßwerte. Eine UV-Bestrahlung von 10 Minuten vermochte zwar die Intensität der mit den Reagenslösungen A/1 bis A/5

Tabelle 2. Einfluß der Höhe des Eisenchloridzusatzes auf die Extinktionen

(Schwefelsäuregehalt des Reagens ~ 75%)
Filter S 61; 0,5 cm Schichtdicke; Reagenslösungen A/1 bis A/8

ml Eisenchloridlösung	0,00	0,01	0,02	0,03	0,05	0,10	0,15	0,20
	Extinktionen							
Lösung 1 (zirka 200 µg Ergotamin/ml)								
30 Minuten Wartezeit (Tageslicht)	0,36	0,52	0,63	0,69	0,79	0,86	0,88	0,88
Zusätzlich 10 Minuten UV-Bestrahlung	0,73	0,78	0,80	0,82	0,85	0,88	0,88	0,88
Lösung 2 (zirka 160 µg Ergotamin/ml)								
30 Minuten Wartezeit (Tageslicht)	0,32	0,40	0,50	0,58	0,69	0,77	0,77	0,77
Zusätzlich 10 Minuten UV-Bestrahlung	0,60	0,63	0,65	0,70	0,73	0,77	0,77	0,77
Lösung 3 (zirka 30 µg Ergotamin/ml)								
30 Minuten Wartezeit (Tageslicht)	0,06	0,11	0,13	0,14	0,14	0,15	0,15	0,15
Zusätzlich 10 Minuten UV-Bestrahlung	0,11	0,14	0,14	0,15	0,15	0,15	0,15	0,15

erzeugten Blaufärbung zu verstärken, es fand jedoch keine Veränderung der Extinktionen bei den Alkaloidlösungen statt, bei denen sich durch Verwendung der Reagenslösung A/6 bis A/8 bereits ohne UV-Bestrahlung die erreichbare Farbtiefe gebildet hatte. Danach muß angenommen werden, daß die Menge des Eisenchlorids bei einigen der in der Literatur angegebenen Reagenslösungen zu gering ist, so daß erst durch Bestrahlung mit der Quecksilberdampflampe volle Farbtiefe erreicht werden kann. Folgende Versuchsreihe sollte hierfür den Beweis bringen. Wurden zu 100 ml 65%iger Schwefelsäure, die 0,2 g des Aldehyds enthielten (Reagenslösung B), wie bei den Reagenslösungen A/1 bis A/8 steigende Mengen Eisenchloridlösung (10 g $FeCl_3 \cdot 6\,H_2O$/100 ml) hinzugefügt, so ergaben sich unter den oben beschriebenen Bedingungen folgende Meßergebnisse (Tabelle 3).

Vergleicht man die Werte der Tabellen 2 und 3, so fällt auf, daß trotz gleicher Eisen- und Aldehydkonzentration* nicht unwesentliche

* Hierbei wurde vernachlässigt, daß sich bei den Reagenslösungen A der Eisensalzzusatz infolge der Kontraktion beim Mischen von Schwefelsäure und Wasser nicht auf genau 100 ml Reagens bezieht.

Tabelle 3. Einfluß der Höhe des Eisenchloridgehaltes auf die Extinktionen

(Schwefelsäuregehalt des Reagens 65%)
Filter S 61; 0,5 cm Schichtdicke; Reagenslösung B/1 bis B/8

ml Eisenchloridlösung	0,00	0,01	0,02	0,03	0,05	0,10	0,15	0,20
	Extinktionen							
Lösung 1 (zirka 200 µg Ergotamin/ml)								
30 Minuten Wartezeit (Tageslicht)	0,50	0,60	0,64	0,65	0,65	0,70	0,75	0,88
Zusätzlich 10 Minuten UV-Bestrahlung	0,73	0,87	0,88	0,89	0,88	0,89	0,89	0,88
Lösung 2 (zirka 160 µg Ergotamin/ml)								
30 Minuten Wartezeit (Tageslicht)	0,29	0,44	0,44	0,46	0,52	0,63	0,77	0,77
Zusätzlich 10 Minuten UV-Bestrahlung	0,61	0,70	0,75	0,76	0,77	0,77	0,77	0,77
Lösung 3 (zirka 30 µg Ergotamin/ml)								
30 Minuten Wartezeit (Tageslicht)	0,06	0,12	0,12	0,12	0,13	0,13	0,14	0,15
Zusätzlich 10 Minuten UV-Bestrahlung	0,12	0,12	0,13	0,14	0,15	0,15	0,15	0,15

Differenzen bei Verwendung der beiden Reagenzien bestehen, so daß bei den Reagenslösungen B eine größere Menge $FeCl_3$ notwendig war, um zu den Endwerten zu gelangen, als bei den Reagenslösungen A. Hierfür muß die unterschiedliche Säurekonzentration (65- und 75%ig) verantwortlich gemacht werden. UV-Licht kann eine nicht ausreichende Eisen(III)-chloridkonzentration weitgehend kompensieren und eine weitere Farbvertiefung herbeiführen, die gegebenenfalls die Ablesung eines Maximalwertes möglich macht. Durch Anwendung von Reagenslösungen mit konstantem Eisengehalt und ansteigendem Schwefelsäuregehalt soll in Tabelle 4 der Einfluß der Säurekonzentration bei der Farbreaktion geklärt werden.

Nach der von *M. Pöhm*[8] gegebenen Deutung der Farbreaktion wird der Schwefelsäure eine Wasserabspaltung zugeschrieben. Es mußte demzufolge erwartet werden, daß mit einem Ansteigen der Schwefelsäurekonzentration dieser Vorgang günstig zu beeinflussen sei, was nach Tabelle 4 auch der Fall ist. Zu hohe Säurekonzentrationen erwiesen sich jedoch als ungeeignet, optimale Werte ergaben sich bei Bereitung des Reagens mit 75- bis 80%iger Schwefelsäure, da ohne UV-Bestrahlung bei

Tabelle 4. Einfluß der Säurekonzentration des Reagens auf den quantitativen Verlauf der Farbreaktion

Zusammensetzung des Reagens: In 100 ml der jeweiligen Schwefelsäure 0,2 g p-Dimethylaminobenzaldehyd gelöst, 0,1 ml Eisenchloridlösung (10% $FeCl_3 \cdot 6\,H_2O$/100 ml) zugesetzt
Filter S 61; 0,5 cm Schichtdicke

Schwefelsäurekonzentrationen	25%	50%	55%	60%	65%	70%	75%	80%	85%
	Extinktionen								
Lösung 1 (zirka 200 µg Ergotamin/ml)									
30 Minuten Wartezeit (Tageslicht)	0,13	0,40	0,49	0,58	0,68	0,77	0,86	0,88	0,85
Zusätzlich 10 Minuten UV-Bestrahlung	0,61	0,88	0,88	0,88	0,88	0,88	0,88	0,88	0,84
Lösung 2 (zirka 160 µg Ergotamin/ml)									
30 Minuten Wartezeit (Tageslicht)	0,13	0,38	0,44	0,52	0,61	0,70	0,77	0,77	0,74
Zusätzlich 10 Minuten UV-Bestrahlung	0,73	0,77	0,77	0,77	0,77	0,77	0,77	0,77	0,74
Lösung 3 (zirka 100 µg Ergotamin/ml)									
30 Minuten Wartezeit (Tageslicht)	0,08	0,24	0,30	0,37	0,42	0,44	0,44	0,44	0,37
Zusätzlich 10 Minuten UV-Bestrahlung	0,27	0,44	0,44	0,44	0,44	0,44	0,44	0,44	0,37

der angegebenen Eisenchloridmenge die volle Extinktion im wesentlichen erreicht werden konnte. Zudem tritt die Blaufärbung bei Zugabe des Reagens nahezu schlagartig auf. Innerhalb von 5 Minuten erreichten die Werte stets ihr Maximum*. Bei Reagenslösungen mit 50- bis 65%iger Schwefelsäure waren unter den angegebenen Bedingungen Höchstwerte ohne weiteres nicht zu messen, doch genügten 10 Minuten Bestrahlung mit der Analysenquarzlampe, um auch bei diesen Säurekonzentrationen zum vollen Blauwert zu gelangen. 25%ige Schwefelsäure erwies sich dagegen in jeder Hinsicht als zu schwach.

Es könnte ferner angenommen werden, daß bei einer zu geringen Eisenchloridmenge, bei der die Reaktion nur langsam und zudem nicht quantitativ verläuft, der Luftsauerstoff oxydativ den chemischen Vorgang

* Wegen der durch Zugabe der schwefelsauren Reagenslösung auftretenden Wärmebildung empfiehlt sich im allgemeinen eine Messung nach 15 Minuten oder später. Die erzeugte Blaufärbung ist relativ stabil. Eine Versuchsreihe, die nach 32 Stunden nochmals photometrisch überprüft wurde, zeigte noch gleiche Meßergebnisse.

unterstützt und mit der Zeit ein allmähliches Ansteigen der Extinktionen bewirkt. Es ist weiterhin naheliegend, daß bei der Bestrahlung mit der Quecksilberdampflampe das hierbei auftretende Ozon als Oxydationsmittel die Wirkung des Eisen(III)-chlorids ergänzt oder ersetzt. Dies ist jedoch nicht der Fall, wie Versuche, bei denen das Reaktionsgemisch unter Stickstoff gehalten wurde, ergaben. Es konnte stets die gleiche Extinktion wie bei Parallelproben ohne Ausschaltung des Sauerstoffes bzw. des Ozons gemessen werden. Hieraus ergibt sich, daß bei der Bestrahlung mit der Analysenlampe allein die Lichteinwirkung die Reaktion aktiviert. Wie eigene Versuche zeigten, handelt es sich bei ausreichenden $FeCl_3$-Mengen und genügender Konzentration der Schwefelsäure um eine rein chemische Reaktion, die unabhängig von jeglicher Lichteinwirkung quantitativ verläuft und innerhalb kürzester Zeit zum vollen Farbwert führt. Eine Abhängigkeit des Reaktionsablaufes vom Licht ist jedoch dann nicht grundsätzlich zu verneinen, wenn dem Reagens zu wenig Eisenchlorid zugefügt war. In diesem Falle lagen die Extinktionen nämlich bei unter Tageslicht aufbewahrten Reaktionsflüssigkeiten höher als bei den unter Ausschluß von Licht durchgeführten Reaktionen.

Demnach ist Eisen(III)-chlorid als Oxydationsmittel an der Farbreaktion beteiligt. Um den quantitativen Ausfall zu gewährleisten, muß dessen Menge ausreichend sein. Diese ist abhängig von dem Alkaloidgehalt der zu prüfenden Lösung sowie von der Stärke der Schwefelsäure. Da eine UV-Bestrahlung, mit der eine zu geringe Säurekonzentration bzw. eine nicht ausreichende $FeCl_3$-Menge kompensiert werden kann, nicht nur das Verfahren kompliziert, sondern unter Umständen zu einem Abfall der Extinktionen führen kann, ist eine derartige Behandlung der Reaktionsflüssigkeit nicht zweckmäßig. UV-Bestrahlung und jegliche Belichtung des Reaktionsgemisches erübrigt sich, wenn ein Reagens folgender Zusammensetzung verwendet wird:

Zu einer Mischung aus 35 ml Wasser und 65 ml konz. Schwefelsäure (entsprechend einer zirka 75 g/g%igen Schwefelsäure) werden 0,2 g p-Dimethylaminobenzaldehyd sowie 0,15 ml einer 10%igen Lösung (g/v) von $FeCl_3 \cdot 6\,H_2O$ gegeben.

Hiermit sind auch Mengen bis zu 1 μg exakt meßbar (Kleinküvetten), so daß die gleiche Reagenslösung auch zur quantitativen Auswertung von Papierchromatogrammen eingesetzt werden kann.

Von den bisher vorgeschlagenen Verfahren zur Bestimmung der Alkaloide auf dem Papier bewährt sich die Methodik nach *M. Pöhm* und *L. Fuchs*[22]. Sollen lediglich die Alkaloidflecken zur Identifizierung der Verbindungen sichtbar gemacht werden, empfiehlt sich die Anfärbetechnik nach *A. Stoll* und *A. Rüegger*[23]. Zunächst sind zweckmäßigerweise die unter ultraviolettem Licht fluoreszierenden Alkaloide mit Bleistift zu markieren. Da Dihydroalkaloide, Lumialkaloide und auch eine Anzahl

Clavine bei Anregung mit dem Ultraviolett der Quecksilberdampflampe keine Fluoreszenz aufweisen, ist auf diese Weise bereits eine Unterscheidung möglich. Nach neueren Angaben von *J. Kolšek*[24] werden jedoch mit dem p-Dimethylaminobenzaldehydreagens keine absoluten Alkaloidmengen erfaßt, wenn zuvor — wie allgemein üblich — die auf dem Papier aufgetrennten Alkaloide zur Identifizierung und zur Fixierung ihrer Lage zunächst unter der UV-Lampe mit Bleistift markiert werden. Nach Angaben von *Kolšek* ist bereits nach einer Belichtung der Alkaloide während 15 Sekunden auf dem Papier ein deutlicher Abfall der Extinktionen der nach *Pöhm* und *Fuchs* gewonnenen Lösungen zu verzeichnen, nach 5 Minuten bereits ein Verlust bis zu 64%. *Kolšek* demonstriert, daß bei der fortschreitenden Zersetzung der Alkaloide unter dem Einfluß der UV-Strahlen das Verhältnis der einzelnen Alkaloide stets konstant bleibt, so daß die photometrisch gemessenen „Blauwerte" lediglich relative Werte darstellen sollen. Wir können die Angaben von *Kolšek* insoweit bestätigen, als eine Zersetzung der Alkaloide auf dem Papier bei direkter Bestrahlung mit einer Quecksilberlampe (Höhensonne), das heißt ohne Zwischenschaltung eines Filters, zu beobachten war (Tabelle 5). Zur Markierung der Alkaloide auf dem Papier wird jedoch allgemein mit gefilterten UV-Strahlen gearbeitet, da bei ungefiltertem Licht keine Fluoreszenz zu beobachten ist. Im wesentlichen werden Filter (UG 1 bis 4) verwendet, die aus dem UV-Spektrum den Wellenbereich um 366 nm isolieren. Hiermit erfolgt jedoch nach unseren Versuchen selbst bei 15minutiger Bestrahlung keine Zersetzung der Alkaloide, so daß die Alkaloide unter der UV-Lampe identifiziert und anschließend photometrisch bestimmt werden können. Der zerstörende Einfluß des ungefilterten Lichtes dürfte den Ultravioletttstrahlen wesentlich geringerer Wellenlängen zuzuschreiben sein.

Zur Aufstellung der Tabelle 5 applizierten wir auf unbehandeltes Papier 2043b (Schleicher & Schüll) Volumenteile einer chloroformigen Ergotaminlösung, wobei die aufgetragenen Alkaloidflecke einheitlich 10 bis 12 mm Durchmesser aufwiesen. Eine Fleckenserie blieb unbehandelt. Eine Serie wurde 5 Minuten lang, eine weitere 15 Minuten lang mit gefiltertem UV-Licht bestrahlt, während die letzte Reihe direkt der Strahlung einer Quecksilberdampflampe, das heißt ohne Zwischenschaltung eines Filters, ausgesetzt war. Die Flecke wurden alsdann ausgeschnitten, zerkleinert und entsprechend den Angaben von *Pöhm* und *Fuchs* mit einem Teil 1%iger Weinsäurelösung und zwei Teilen des oben beschriebenen Reagens bis zur Zerfaserung geschüttelt. Die abgenutschte blaue Farblösung wurde photometriert. Parallel dazu pipettierten wir entsprechende Volumenteile der Alkaloidlösung in Schälchen, ließen das Lösungsmittel verdunsten und bestimmten die Alkaloidmengen gleichfalls photometrisch.

Tabelle 5. Einfluß von UV-Bestrahlung auf die Zersetzung der Alkaloide auf dem Papier

Alkaloidlösung: Ergotamin in chloroformiger Lösung
Papier: Unbehandeltes S & S 2043 b
Quarz-Quecksilberdampflampe: „Elmed-Lumina-U" (VEB Elmed, Hohen-Neuendorf)
Filter: UG 4 (Wellenbereich um 366 nm)
Abstand der Alkaloidflecken vom Filter: 20 cm
Photometrische Farbmessung: Filter S 61; Schichtdicke 0,5 cm

Volumenteile einer Alkaloidlösung	Schälchen unbestrahlt	Papier			
		unbestrahlt	bestrahlt mit Filter 5 Minuten	bestrahlt mit Filter 15 Minuten	bestrahlt ohne Filter 5 Minuten
		Extinktionswerte			
1	0,05	0,05	0,05	0,05	0,03
2	0,10	0,10	0,10	0,10	0,05
3	0,15	0,15	0,15	0,15	0,11
4	0,20	0,20	0,20	0,20	0,15
5	0,25	0,25	0,25	0,25	0,19
6	0,30	0,30	0,30	0,30	0,20

Völlig übereinstimmende Ergebnisse ließen sich zudem auf mit 0,2%iger Weinsäurelösung getränktem Papier[20,21] erzielen. Bei Verwendung von Papieren, die nach Tränkung mit 50%iger äthanolischer Formamidlösung behandelt und alsdann zwischen Filterpapier abgepreßt waren, ergaben sich keinerlei Unterschiede in den Extinktionen*. Selbst Überprüfungen anderer Analysenquarzlampen und anderer Filter** bestätigten lediglich die in Tabelle 5 aufgeführten Ergebnisse.

Fräulein *Waltraud Kretschmer* danke ich auch an dieser Stelle für ihre zuverlässige Hilfe.

Zusammenfassung

Die unterschiedliche Zusammensetzung der gebräuchlichen p-Dimethylaminobenzaldehydreagenslösungen zum Nachweis und zur Bestimmung der Mutterkornalkaloide gewährleistet nicht immer einen quantitativen Verlauf der Farbreaktion. Die Abhängigkeit der Reaktion

* Da Formamidstreifen gewöhnlich noch im „klammfeuchten" Zustand unter UV-Licht ausgewertet werden, bei unserem Modellversuch das Papier jedoch durch Verwendung eines Trockengerätes (Föhn) beim Auftragen der Alkaloidlösung praktisch trocken war, besprühten wir es vor der Bestrahlung mit der Quecksilberdampflampe nochmals mit äthanolischer Formamidlösung.

** Asta-Analysenquarzlampe der Firma A. W. Steinmann, Allersdorf-Königsee/Thür. Filter UG 1, UG 2, UG 3, UG 4, UG 5. (Abstand vom Filter: 30 cm, Bestrahlungsdauer 5 Minuten.)

vom Alkaloidgehalt der zu messenden Lösungen, von der Säurekonzentration des Reagens und von der Menge des als Oxydationsmittel zugesetzten Eisen(III)-chlorids wurde überprüft, sowie der Einfluß von Licht, insbesondere von UV-Strahlung auf die Erzielung maximaler Extinktionswerte studiert. Eine eigens hierfür angegebene Reagenslösung ist für photometrische Bestimmungen von Mutterkornalkaloiden geeignet. Die allgemein übliche Markierung der im gefilterten UV-Licht der Quecksilberdampflampe fluoreszierenden Alkaloidflecke beim papierchromatographischen Nachweis ist ohne Einfluß auf die photometrisch zu ermittelnden Meßergebnisse.

Summary

The divergent composition of the ordinary *p*-dimethylaminobenzaldehyde reagent solutions used for the detection and determination of the ergot alkaloids does not always insure that the color reaction will proceed quantitatively. A study was made of the dependence of the reaction on the alkaloid content of the solutions to be measured, on the acid concentration of the reagent, and on the amount of ferric chloride added as oxidizing agent. The influence of light, particularly ultraviolet radiation, was studied with respect to the achievement of maximum extinction values. A reagent solution prescribed expressly for this purpose is suitable for the determination of ergot alkaloids. The generally employed marking of the alkaloid flecks that fluoresce in filtered UV light of the mercury lamp as employed in the chromatographic detection has no influence on the measurements obtained photometrically.

Résumé

La composition différente des solutions usuelles de *p*-diméthylaminobenzaldéhyde utilisée pour l'identification et le dosage des alcaloïdes de l'ergot de seigle n'assurent pas toujours une évolution quantitative de la réaction colorée. L'auteur a contrôlé la dépendance de la réaction de la teneur en alcaloïdes de la solution à mesurer, de la concentration en acide du réactif et de la quantité de chlorure ferrique introduit comme réactif oxydant; il a étudié d'autre part l'influence de la lumière en particulier du rayonnement ultraviolet sur l'obtention de valeurs d'extinction maximales. Une composition de réactif indiquée particulièrement à cette fin est appropriée aux dosages photométriques des alcaloïdes de l'ergot de seigle. Le marquage habituellement employé de la tache d'alcaloïde fluorescente dans la lumière ultraviolette filtrée de la lampe à vapeur de mercure, obtenue pour identification par chromatographie sur papier, est sans influence sur les résultats de mesures obtenus par photométrie.

Literatur

[1] *H. W. van Urk*, Pharmac. Weekbl. **66**, 473 (1929).

[2] *M. I. Smith*, U. S. A. Publ. Health Rep. **45**, 1466 (1930).

[3] *N. L. Allport* und *T. T. Cocking*, Quart. J. Pharmac. Pharmacol. **5**, 341 (1932).

[4] *E. Schulek* und *G. Vastagh*, Dansk Tidsskr. Farmaci **13**, 101—105 (1939).

[5] *I. Molnár* und *A. Uskert*, Magyar. Kemiai Folyoirat **56**, 230 (1950), zitiert nach Chem. Zbl. **1951**, 2929.
[6] *P. Tuzson, J. Tuzson* und *J. Bayer*, Acta Chim. Acad. Sci. Hung. **2**, 15 (1951).
[7] *J. Tuzson* und *G. Vastagh*, Pharmac. Acta Helv. **29**, 118 (1954).
[8] *M. Pöhm*, Arch. Pharmaz. **286**, 509 (1953).
[9] *A. Silber* und *T. Schulze*, Pharmazie **8**, 675 (1953).
[10] *L. C. Schramm*, J. Amer. Pharmac. Assoc., Sci. Ed. **47**, 326—329 (1958).
[11] *K. H. Renneberg*, Arch. Pharmaz. **291**, 408 (1958).
[12] *J. Kolšek*, Mikrochim. Acta [Wien] **1956**, 1377.
[13] *H. Rochelmeyer, E. Stahl* und *A. Patani*, Arch. Pharmaz. **291**, 1 (1958).
[14] *L. Fuchs* und *W. Himmelbauer*, Scientia Pharmac. **18**, 93 (1950).
[15] *L. Fuchs, M. Hecht* und *M. Pöhm*, Scientia Pharmac. **21**, 350 (1953).
[16] *G. Schumacher*, Dtsch. Apothek.-Ztg. **55**, 312 (1940).
[17] *I. Corubolo* und *M. Grims*, Pharmazie **10**, 60 (1955).
[18] *R. Fischer* und *M. Hecht*, Mikrochem. **38**, 538 (1951).
[19] *E. Thielmann, W. Lang* und *H. Kaiser*, Arch. Pharmaz. **286**, 379 (1953).
[20] *R. Voigt* und *F. Weiß*, Pharmazie **13**, 212 (1958).
[21] *R. Voigt*, Pharmazie **13**, 294 (1958).
[22] *M. Pöhm* und *L. Fuchs*, Naturwiss. **40**, 244 (1953).
[23] *A. Stoll* und *A. Rüegger*, Helv. Chim. Acta **37**, 1725 (1954).
[24] *J. Kolšek*, Mikrochim. Acta [Wien] **1956**, 1500.

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Über eine einfache Schnellmethode der Stickstoffmikrobestimmung nach Dumas

Von

Kurt Eder

Mit 1 Abbildung

(Eingegangen am 11. März 1959)

Bei der üblichen Stickstoffmikrobestimmung nach Dumas ist für die Verbrennungsphase eine Blasengeschwindigkeit von zwei Blasen in 3 Sekunden vorgeschrieben[1]. Wird diese überschritten, was bei sehr zersetzlichen Substanzen leicht der Fall sein kann, so ist mit fehlerhaften Analysenwerten zu rechnen.

W. Zimmermann[2] hat nun gefunden, daß die Verbrennungsgeschwindigkeit keinen Einfluß auf das Resultat hat, wenn man die Verbrennungsgase bei geschlossenem Azotometerhahn zunächst in ein mit Quecksilber gefülltes Gassammelgefäß leitet, das sich zwischen dem Verbrennungsrohr und dem Kohlensäure-Entwicklungsgefäß befindet, und nach beendeter Verbrennung der Substanz die Verbrennungsgase durch das Verbrennungsrohr in das Azotometer drückt und mit Kohlensäure nachspült.

Zimmermann vermutet, daß durch die Verdünnung der Verbrennungsgase mit Kohlendioxyd eine vollständige Verbrennung auch bei kurzer Berührungsdauer der Gase mit der heißen Rohrfüllung erzielt wird. Man kann aber auch annehmen, daß bei der Zimmermannschen Anordnung eine „Vorverbrennung" stattfindet, da ja die Verbrennungsgase auf ihrem Weg zum Sammelgefäß zunächst eine durch den Kurzbrenner erhitzte Zone von Kupferoxyd passieren müssen, wobei bereits eine mehr oder weniger weitgehende Oxydation der Verbrennungsprodukte stattfindet. Dies ist insofern wahrscheinlich, als sonst mit dem Auftreten teeriger Zersetzungsprodukte im leeren, kalten Teil des Verbrennungsrohres zu rechnen wäre.

Auf Grund dieser Überlegung wurde nun versucht, durch eine kleine Änderung der Verbrennungstechnik ohne Zuhilfenahme des Sammelgefäßes die Verbrennung ebenso rasch wie nach *Zimmermann* durchzuführen. Die unten angeführten Beleganalysen (Tabelle 1) zeigen, daß dies möglich ist. Gegenüber dem sonst üblichen Verfahren benötigt man nur etwas mehr Kupferoxyd und einen zweiten Kurzbrenner. Die Anordnung der Apparatur ist aus der folgenden Skizze zu ersehen (Abb. 1).

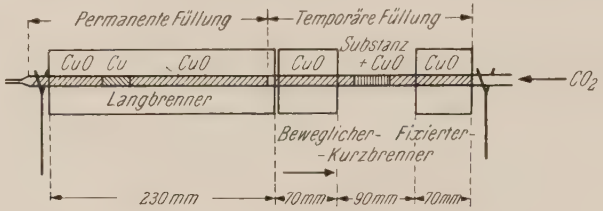

Abb. 1

Für die Versuche wurde ein Verbrennungsautomat von Hösli* mit einem Langbrenner von 23 cm und einem Kurzbrenner von 7 cm Länge verwendet. Als zweiter Kurzbrenner wurde ebenfalls ein elektrisch geheizter Brenner von 7 cm Länge angebracht. Die Länge des Verbrennungsrohres betrug 55 cm.

Tabelle 1. Beleganalysen

Substanz	% N	
	gef.	ber.
Acetanilid	10,42	10,38
Harnstoff	46,77	46,67
Diphenylamin.....	8,31	8,28
$C_9H_9ON_3$	23,91	23,97
$C_{17}H_{23}O_2N$	5,09	5,13
$C_{16}H_{19}O_3N$	5,21	5,12
$C_{16}H_{15}O_3N$	5,20	5,20
$C_9H_{10}ON_2S$	14,35	14,42
$C_{30}H_{44}O_4N_2Cl_2$	4,88	4,94
$C_{16}H_{18}O_2N_4$	18,80	18,77
$C_{31}H_{47}O_{10}N_3$	6,85	6,76

Das Prinzip der Methode besteht darin, daß man den beweglichen Kurzbrenner aus seiner Ausgangsstellung direkt neben dem Langbrenner in Gegenstromrichtung bei offenem Azotometerhahn an die Substanz heranführt. Die Verbrennungsgase müssen auf ihrem Weg zum Azoto-

* Bischofszell, Schweiz.

meter zunächst die durch den beweglichen Kurzbrenner erhitzte Zone von Kupferoxyd durchlaufen, wo bereits eine weitgehende Oxydation der Verbrennungsprodukte stattfindet. Nach Passieren einer kurzen, kühleren Zone zwischen Langbrenner und Kurzbrenner erfolgt die vollständige Oxydation in der langen heißen Zone, ehe die Gase in das Azotometer eintreten. Zur Verhinderung des Zurückwanderns unvollständig verbrannter Zersetzungsprodukte in den leeren Teil des Verbrennungsrohres dient der zweite, fixiert gehaltene Kurzbrenner. Bei der Füllung des Verbrennungsrohres mit der temporären Schicht Kupferoxyd ist darauf zu achten, daß die Substanz in die Mitte zwischen die beiden Kurzbrenner zu liegen kommt.

Ausführung der Verbrennung

Zum Ausspülen des mit der Substanz beschickten Verbrennungsrohres wird zunächst 2 Minuten lang ein mäßig rascher Strom von Kohlendioxyd durch das kalte Verbrennungsrohr geleitet. Dann wird der heiße Langbrenner über das Verbrennungsrohr geschoben und das Ausspülen eine Minute lang fortgesetzt. Nach dieser Zeit ist das Verbrennungsrohr normalerweise luftfrei, zumal durch die längere Rohrfüllung der leere Teil des Verbrennungsrohres verkleinert ist. Dann wird das Azotometer angeschlossen und das Einleitungsrohr des Azotometers luftfrei gespült. Sobald Mikroblasen erhalten werden, wird das Azotometer aufgefüllt und die beiden bereits heißen Kurzbrenner in ihre entsprechenden Stellungen über das Verbrennungsrohr gebracht: den beweglichen Kurzbrenner direkt neben den Langbrenner und den stationären Kurzbrenner über das Ende der Rohrfüllung (s. Abb. 1). Nach etwa 2 bis 3 Minuten sind auch diese Teile des Verbrennungsrohres heiß genug, daß mit der Verbrennung begonnen werden kann. Man schiebt den beweglichen Brenner in Gegenstromrichtung an die Substanz und verbrennt in zügigem Tempo, wobei nur darauf zu achten ist, daß die Gasbläschen mit etwas Abstand aufsteigen, damit sie sich nicht etwa im Azotometer zu größeren Blasen vereinigen und hängen bleiben. Die eigentliche Verbrennung läßt sich je nach Stickstoffgehalt in 5 bis 8 Minuten durchführen; zum Nachspülen bei gleicher oder leicht erhöhter Blasenfrequenz werden etwa weitere 3 bis 5 Minuten benötigt. Die Verbrennungsgeschwindigkeit bei den Versuchen betrug etwa eine Blase pro Sekunde, zum Nachspülen wurde die Geschwindigkeit auf etwa zehn Blasen in 8 Sekunden erhöht.

Bei Verwendung eines automatischen, umkehrbar beweglichen, entsprechend raschen Vorschubes, ließe sich die Verbrennung unbeaufsichtigt durchführen. Während für eine Analyse etwa 15 Minuten gebraucht werden, beansprucht das Auskühlenlassen des Verbrennungsrohres verhältnismäßig viel Zeit. Diese könnte jedoch durch entsprechende Konstruktion der Verbrennungsautomaten wesentlich herabgesetzt werden.

Zusammenfassung

Durch die beschriebene Änderung der Verbrennungstechnik läßt sich der für eine Stickstoffmikrobestimmung nach Dumas-Pregl erforderliche Zeitaufwand wesentlich herabsetzen.

Summary

The modification of the combustion technique described here results in a considerable saving in time required for the Dumas-Pregl microdetermination of nitrogen.

Résumé

Description d'une modification de la technique de combustion permettant une diminution considérable du temps nécessaire à la microdétermination de l'azote par la méthode de Dumas-Pregl.

Literatur

[1] *Pregl-Roth*, Quantitative organische Mikroanalyse, 7. Aufl. von Dr. *H. Roth*. Wien: Springer-Verlag. 1958. S. 91.

[2] *W. Zimmermann*, Mikrochem. **31**, 42 (1943).

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Studies in Qualitative Inorganic Analysis. XII*

A Comparison of the Methods Used in the Group Separation of Strontium and Calcium Ions

By

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After barium has been precipitated as chromate in acetic acid solution in the calcium group, the various reagents which are used to separate calcium and strontium are:

1. Saturated ammonium sulphate solution**, which precipitates strontium sulphate, but forms soluble calcium ammonium sulphate with calcium ions,

2. Saturated calcium sulphate solution**,

3. Potassium chromate solution[1], which, in the presence of ammonia and ethanol, forms insoluble strontium chromate, calcium remaining in solution and being subsequently detected with ammonium oxalate.

The purpose of this investigation was to examine the relative efficiency of these reagents.

This was done by first carrying out sensitivity tests. These determine:

1. the amount of strontium which remains in solution and which is carried over to interfere with the test for calcium,

2. the concentration of calcium ions which co-precipitate with strontium,

3. the precipitant which has the highest sensitivity to strontium.

Confirmatory tests were carried out on mixtures containing different proportions of the two ions, and finally the full group separation was examined.

The results obtained show that the best separation is effected when potassium chromate is used as the precipitant. By the addition of just

* Part XI: Mikrochim. Acta [Wien] **1959**, 554.

** The origins of these methods have not been traced. They are given without reference in most textbooks of qualitative analysis.

sufficient ethanol, strontium is almost completely precipitated. The small amount which remains in solution does not interfere in the calcium test because monochloracetic acid is added; strontium oxalate is not precipitated at the resulting p_H.

Experimental

Sensitivity tests. The figures quoted are the minimum concentration in mg/ml of calcium or strontium which precipitates. Sensitivity tests using the following reagents were made.

A. Ammonium oxalate

Test: To 1 ml of solution add 2 drops of saturated ammonium oxalate solution, warm and stand 5 minutes.

	Sr	Ca
With no other reagent	0.05	0.01
With 1 drop 4 *N* acetic acid	0.05	—
With 3 drops 4 *N* acetic acid	0.08	—
With 1 drop 4 *N* chloracetic acid	0.35	0.05
With 1 drop 4 *N* chloracetic acid and 5–10 drops 5% K_2CrO_4	0.20	0.05
With 1 ml saturated ammonium sulphate	—	0.5

It is seen that:

1. the sensitivity of calcium to ammonium oxalate is considerably reduced in the presence of ammonium sulphate, and

2. the presence of chloracetic acid has only a slight effect on the sensitivity of the test for calcium.

B. Ammonium sulphate

Test: To 1 ml of solution add 1 ml of saturated ammonium sulphate solution, boil and stand 5 minutes.

Sr 0.30 Ca 3.0

Thus Calcium, when present in moderate concentration, will also form a precipitate with this reagent.

C. Calcium sulphate

Test: To 1 ml of solution add 1 ml of saturated calcium sulphate solution, boil and stand 5 minutes.

Sr 0.35

The result shows strontium to be rather less sensitive to this reagent than to ammonium sulphate.

D. Potassium chromate

Test: To 1 ml of solution add 1 drop 4 *N* ammonia and 5–10 drops 5% potassium chromate followed by ethanol. Boil and stand 5 minutes.

It is therefore possible, by careful addition of ethanol, to prevent any precipitation of calcium, within the limit of any concentration encountered on the semi-micro scale. The tests also show that:

Volume of ethanol	Sr	Ca
2.0 ml	0.01	0.5
1.0 ml	0.03	1.5
0.75 ml	0.06	5.0
0.50 ml	0.15	20.0*

* No precipitate.

1. the concentration of strontium remaining in solution is less than will affect the test for calcium in the presence of chloracetic acid, and

2. potassium chromate, in ammonia solution, is the most sensitive reagent for the precipitation of strontium.

Confirmatory

The following separations were carried out:

1. To 1 ml of the mixed solution containing 0.3 mg strontium (i. e. the sensitivity limit of strontium to saturated ammonium sulphate) and 0.05 mg calcium, add 1 ml of saturated ammonium sulphate, boil, stand 5 minutes and centrifuge. To the solution add 1 drop of 4 *N* chloracetic acid, 2 drops of saturated ammonium oxalate, warm and stand 5 minutes. Repeat the test after increasing the concentration of calcium by 0.05 mg each time.

The minimum concentration of calcium which precipitated was 0.5 mg/ml.

2. To 1 ml of solution containing varying amounts of strontium and calcium, add 1 drop of 4 *N* ammonia, 5–10 drops of potassium chromate and 0.5 ml of ethanol. Boil and stand 5 minutes. Centrifuge. Add 1 drop of 4 *N* chloracetic acid, 2 drops of ammonium oxalate, warm and stand 5 minutes.

Mixture	Sr	Result	Ca	Result
1	nil	—	0.05	+
2	0.1	—	nil	—
3	0.1	—	nil	+*
4	0.2	+	0.05	+
5	0.5	+	nil	—
6	0.5	+	0.05	+
7	1.0	+	0.05	+
8	10.0	+	nil	—
9	10.0	+	0.10	+

* No chloracetic acid added.

It is seen that the extent of co-precipitation by calcium with strontium is very small.

Group Separation

The following scheme was adopted using the potassium chromate reagent:

Add to the solution obtained after removal of lead[2], 10 drops of 5% K_2CrO_4. Warm and centrifuge.

Residue	Solution
$BaCrO_4$ Test for barium	Boil 1–2 minutes to reduce volume to approximately 1 ml (note 1). Make alkaline by adding 3 drops of 4 *N* ammonia and add a further 5 drops of potassium chromate solution, followed by 0.5 ml of ethanol (note 2). Stir while bringing to the boil, stand 5 minutes and centrifuge

Residue	Solution
$SrCrO_4$ Test for strontium	Boil 1–2 minutes to remove ethanol, dilute with an equal volume of water and add 3 drops of 4 *N* chloracetic acid (note 3). Add 2 drops of saturated ammonium oxalate, warm and stand 5 minutes. A white crystalline precipitate shows the presence of calcium

Note 1. If the volume exceeds 1 ml some strontium escapes precipitation and affects the subsequent test for calcium.

Note 2. The volume of ethanol must be accurately measured. Too large a volume results in the precipitation of calcium. If insufficient is added some strontium remains in solution.

Note 3. The removal of ethanol, dilution and addition of chloracetic acid, prevent the precipitation of the small amount of strontium carried over.

This separation has proved satisfactory for solutions of mixtures of ions of the following concentrations:

Mixture	Ba	Sr	Ca
1	10.0	—	—
2	10.0	0.15	—
3	10.0	10.0	—
4	10.0	10.0	0.1
5	10.0	—	10.0
6	—	10.0	—
7	—	—	20.0

Summary

Potassium chromate is a more sensitive and a more selective reagent in the group separation of strontium and calcium than others which are in use for this purpose. Ammonium sulphate is not recommended because it seriously affects the sensitivity of calcium ions to ammonium oxalate.

Zusammenfassung

Im Vergleich zu anderen, für die Trennung von Strontium und Calcium im qualitativen Analysengang gebräuchlichen Reagenzien, ist Kaliumchromat empfindlicher und selektiver. Ammoniumsulfat kann für diesen Zweck nicht empfohlen werden, da es die Empfindlichkeit des Calciumnachweises mit Ammoniumoxalat stark beeinträchtigt.

Résumé

Le chromate de potassium est un réactif plus sensible et plus sélectif, pour la séparation par groupe du strontium et du calcium, que d'autres réactifs utilisés à cette fin. Le sulfate d'ammonium n'est pas recommandé car il exerce une influence préjudiciable à la sensibilité des ions calcium à l'oxalate d'ammonium.

References

[1] *W. Fresenius* and *F. Ruppert*, Z. analyt. Chem. **30**, 677 (1891); cf. *W. C. Bray*, J. Amer. Chem. Soc. **31**, 615 (1909).

[2] Midlands Association for Qualitative Analysis, "Semi-micro Qualitative Inorganic Analysis, Advanced Tables", 4th Edition. Birmingham. 1959. (Obtainable from Stanford and Mann Ltd., 72–73 New Street, Birmingham 2, 7s. inc. postage.)

Ammoniaklaboratorium/Analytisches Laboratorium der Badischen Anilin- & Soda-Fabrik A. G., Ludwigshafen/Rhein

Beitrag zur mikroanalytischen Schnellbestimmung von Elementen in organischen Substanzen mit der Kolbenmethode. II*: Bestimmung von Arsen

Von

W. Merz

(Eingegangen am 27. März 1959)

Grundlagen zur Methodik des Aufschlusses

Wie in einer vorhergehenden Veröffentlichung[1] berichtet wurde, ließ sich die von *Schöniger*[2] zur Bestimmung von Schwefel und Halogenen in die Mikroanalyse eingeführte Methode zur Verbrennung organischer Substanzen in einem mit Sauerstoff gefüllten Erlenmeyerkolben („Kolbenmethode") auch auf die Bestimmung des Phosphorgehaltes ausdehnen. Daß dieses Aufschlußverfahren selbst bei schwer mineralisierbaren organischen Phosphorverbindungen anwendbar ist, wurde durch Veröffentlichungen von *Fleischer* und Mitarbeitern[3], *Cohen* und *Czech*[4] sowie *Belcher* und *Macdonald*[5] bestätigt.

In der Zwischenzeit veröffentlichten *Southworth* und Mitarbeiter[6] ihre Ergebnisse bei der Anwendung der Methode zur Verbrennung von Organoquecksilberverbindungen. Danach ist der Gehalt an Quecksilber in solchen Verbindungen einwandfrei bestimmbar. *Belcher*, *Macdonald* und *West*[7] berichteten in einer vorläufigen Veröffentlichung über orientierende Versuche zur allgemeinen Anwendbarkeit der Kolbenmethode bei der Ermittlung des Metallgehaltes in metallorganischen Verbindungen. Ausführliche Angaben finden sich hier über die Bestimmung von Zink, Magnesium, Cadmium und Bor. Die Endbestimmung dieser Metalle erfolgt dabei nach Möglichkeit durch Titration mit EDTA.

Bei der Verbrennung von *Organoarsenverbindungen* fanden jedoch diese Forscher keinen Vorteil gegenüber der Methode von *Schulek* und *Villecz*[8], da die zu Beginn der Verbrennung eintretende Legierungs-

* I. Mitteilung: Mikrochim. Acta [Wien] **1959**, 456.

bildung zwischen Arsen und Platin nach ihren Angaben zu größeren Arsenverlusten führt. Etwas bessere, aber immer noch zu niedere Werte fanden *Belcher* und Mitarbeiter[7] durch Imprägnierung des Filtrierpapieres, in dem die Substanzeinwaage eingewickelt wird, mit Kaliumnitrat.

Schon längere Zeit vor der Veröffentlichung dieser Untersuchungen haben auch wir uns mit dem Problem der allgemeinen Anwendbarkeit der Kolbenmethode zur Mikro- und Spurenbestimmung von Metallen in Organometallverbindungen beschäftigt. Der große Vorteil dieses Verfahrens liegt ja nicht nur in seiner Schnelligkeit, sondern vor allem auch darin, daß durch den Aufschluß keine die Endbestimmung störenden Verunreinigungen und Ballastsalze eingeschleppt werden.

Wie aber auch wir im Verlaufe unserer Arbeiten feststellen mußten, scheitert die universelle Anwendung des Aufschlusses in der von *Schöniger*[2] veröffentlichten Form an einer bei zahlreichen Metallen auftretenden Legierungsbildung mit dem Platin. Im Moment der Zündung dürfte sich an der Oberfläche des Platindrahtes bzw. Platinnetzes eine reduzierende Schicht ausbilden, die die Reduktion einer geringen Menge der metallischen Anteile in den nullwertigen Zustand bewirkt und so die Bildung einer Legierung auslöst. Besonders augenfällig ist dies bei der Verbrennung von Organozinnverbindungen, z. B. Triphenylzinnchlorid. Die Legierungsbildung bewirkt hier schließlich eine besonders starke Rekristallisation. Dies führt meist zu einer völligen Zerstörung des Platinnetzes.

Die von *Belcher* und Mitarbeitern[7] beschriebene Legierungsbildung mit Arsen wurde auch von uns beobachtet und ist ja als solche aus zahlreichen Literaturangaben schon lange bekannt. Durch Verwendung von sogenanntem „phosphorbeständigem" Platin, das die platinverarbeitende Industrie unter verschiedenen Bezeichnungen in den Handel bringt, konnten wir aber auch bei der Verbrennung arsenhaltiger Substanzen Werte erhalten, die innerhalb der Fehlergrenze von $\pm$ 0,2% lagen. Die in diesem Falle von dem Platin aufgenommenen Arsenmengen lagen, wie wir durch spektroskopische Untersuchungen feststellen konnten, selbst nach einer größeren Anzahl von Aufschlüssen nicht über 0,001%, was auf die Gewichtsbilanz einer Mikrobestimmung ohne Einfluß ist.

Um aber auch bei Spurenanalysen jeglichen Arsenverlust durch Legierungsbildung auszuschalten, und anderseits eine solche durch anwesende Verunreinigungen oder als weitere Hauptbestandteile vorhandene Elemente zu vermeiden, haben wir versucht, das Platindrahtnetz als Halterung für die Substanzeinwaage durch eine ähnliche Vorrichtung aus Quarz zu ersetzen. Schon die ersten orientierenden Versuche zeigten, daß dies prinzipiell möglich ist. Die bisher allgemein angenommene und auch von *Belcher* und Mitarbeitern[7] dem Platin zuerkannte, spezielle katalytische Wirksamkeit bei der Verbrennung organischer Stoffe ist demnach bei diesem Aufschlußverfahren nicht ausschlaggebend.

Die in der ersten Mitteilung[1] zur Bestimmung des Phosphors angestellten Versuche wurden unter Verwendung von Quarz an Stelle des Platins wiederholt und führten zu denselben exakten Ergebnissen. Dies trifft in der gleichen Weise auf die Analysen arsenhaltiger Verbindungen zu. Auch die Bestimmungen von Halogenen und Schwefel sind nach einer privaten Mitteilung von Herrn Dr. *Huber* (BASF) mittels einer Haltevorrichtung aus Quarz einwandfrei durchführbar. Aus den Ergebnissen dieser eingehenden Untersuchungen kann geschlossen werden, daß durch die Verwendung von Quarz an Stelle des Platins eine wesentlich größere Anwendungsbreite der Kolbenmethode gegeben ist. Dabei empfiehlt es sich, den die Halterung tragenden Stopfen ebenfalls aus Quarz zu fertigen. Der Erlenmeyerkolben selbst kann aus Glas oder Quarz sein.

Im Rahmen dieser Arbeit soll aber auf diese Versuche nur soweit eingegangen werden, als es die Bestimmung des Arsens betrifft. Über weitere Untersuchungen in dieser Richtung soll gesondert berichtet werden.

Ausführung der Arsenbestimmung

Die Verbrennung organischer Arsenverbindungen wird in einem Erlenmeyerkolben aus Glas oder Quarz ausgeführt. Die Haltevorrichtung muß in jedem Falle aus Quarz sein, während der die Halterung tragende Stopfen nach Belieben aus Glas oder Quarz gefertigt sein kann. Wie aber bereits einleitend erwähnt, kann auch sogenanntes phosphorbeständiges Platin zum Aufschluß reiner arsenhaltiger Substanzen verwendet werden. Mit beiden Materialien werden exakte Ergebnisse erhalten. Eine Imprägnierung des Filtrierpapieres mit Kaliumnitrat, wie sie von *Belcher*[7] empfohlen wird, erübrigt sich demnach. Ist jedoch bei Analysen technischer Produkte mit legierungsfähigen, metallischen Verunreinigungen oder gar Hauptbestandteilen zu rechnen, so ist unbedingt Quarz zu verwenden.

Der Endbestimmung des Arsengehaltes wurde große Aufmerksamkeit geschenkt und die einzelnen Methoden eingehend untersucht. Die zahlreichen Modifikationen der jodometrischen Bestimmung sind zufolge ihrer Störanfälligkeit sowohl für Serienanalysen als auch für Spurenbestimmungen wenig verläßlich. Wesentlich günstiger sind in diesem Falle die Bromatmethode[8], insbesondere bei Ausführung als potentiometrische Titration, und die Chinolinmethode[5,9]. Als Schnellmethode bei gleichzeitig hoher Empfindlichkeit und auch Genauigkeit ist jedoch das kolorimetrische Bestimmungsverfahren über den Arsenmolybdänblau-Komplex allen anderen Methoden vorzuziehen. *Kingsley* und *Schaffert*[10] und vor allem *Crawford, Palmer* und *Wood*[11] haben die genauen Bedingungen zur Bildung der Arsenmolybdänsäure und Reduktion dieser Heteropolysäure mit Hydrazinsulfat zu Arsenmolybdänblau eingehend studiert.

Unter Berücksichtigung der Ergebnisse dieser grundlegenden Arbeiten war es möglich, die photometrische Endbestimmung des Arsengehaltes durch Auswahl entsprechender Wellenlängen sowohl im Halbmikro- als auch im Mikrobereich und in der Spurenanalyse universell anzuwenden. Das Maximum der Extinktionskurve liegt bei 835 nm. Extrem niedere Arsengehalte werden in einem Spektralphotometer bei dieser Wellenlänge gemessen. Für Arsengehalte über 10 μg verwenden wir ein Filterphotometer und messen für den Bereich von 10 bis 100 μg unter Verwendung des Filters Hg 691 und über 100 μg mit dem Filter Hg 578, da bei diesen Wellenlängen die molare Extinktion wesentlich niedriger ist als im Maximum. Man kann dadurch ohne Verdünnung den Meßbereich auf höhere Konzentrationen ausdehnen. Eine zur Ablesung der Extinktion erforderliche Farbintensität kann zudem durch Anwendung größerer Schichtdicken oder durch Verkleinerung des Endvolumens erreicht werden. Der der Extinktion entsprechende Arsengehalt wird einer unter gleichen Bedingungen (Wellenlänge und Schichtdicke) aufgestellten Eichkurve entnommen.

Nach der Verbrennung liegt ein großer Teil des Arsens — wie auch *Belcher* und Mitarbeiter[7] festgestellt haben — als Arsen(III) vor. Zur Bildung der Heteropolysäure ist aber nur Arsen(V) fähig, weshalb der Endbestimmung eine Oxydation vorangehen muß. Aus diesem Grunde absorbieren wir die Verbrennungsgase in stark verdünnter, wäßriger Jodlösung. Diese hat den Vorteil, daß sie im Überschuß auf die photometrische Endbestimmung nicht störend wirkt, so daß die oft mühevolle und zeitraubende Entfernung des Oxydationsmittels wegfällt.

Zur Endbestimmung wird die jodhaltige Absorptionslösung mit Ammoniummolybdat und Hydrazinsulfat versetzt, zur Farbentwicklung kurz erwärmt und nach Abkühlen gegen einen analog angesetzten Blindwert gemessen.

Während der Drucklegung dieser Arbeit wurde eine Veröffentlichung von *Corner*[12] bekannt, die sich unter anderem auch mit der Analyse arsenorganischer Verbingungen befaßt, sich aber weitgehend von unserer Arbeitsweise unterscheidet.

Reagenzien und Geräte

Sauerstoff, aus einer Stahlflasche.

Absorptionslösung: etwa 0,01-n Jodlösung, hergestellt durch Lösen von 1,27 g J_2 und 4 g KJ in 1000 ml dest. H_2O (dunkel aufbewahren).

Molybdatlösung: 1%ig in 2,5-n H_2SO_4 (10 g Ammoniummolybdat $[(NH_4)_6Mo_7O_{24} \cdot 4\,H_2O]$ werden in 500 ml 5-n H_2SO_4 (arsenfrei) gelöst und mit dest. H_2O auf 1000 ml verdünnt).

Reduktionslösung: 0,5%ige wäßrige Lösung von $N_2H_4 \cdot H_2SO_4$.

Als *Aufschlußgefäß* dient zur Mikrobestimmung ein 300-ml-, zur Halbmikrobestimmung ein 500-ml-Erlenmeyerkolben aus Glas oder Quarz mit Schliffstopfen, in den ein etwa 75 bzw. 100 mm langer und 3 bis 5 mm starker Quarzstab eingesetzt ist. Dieser ist zum Befestigen des eingerollten Filtrierpapieres am unteren Ende auf 1,5 bis 2 mm ausgezogen und zu einem Haken aufgebogen. Sehr bewährt hat sich auch die Form einer Spirale*.

Als *Filtrierpapier* zum Einwickeln der eingewogenen Substanz sind nur aschefreie Sorten zu benutzen.

Die *Messungen* wurden in einem Spektralphotometer der Firma Carl Zeiss, Modell „PMQ II" bzw. in einem Filterphotometer der Firma Netheler und Hinz, Modell „Eppendorf" ausgeführt.

Arbeitsvorschrift

Einwaage und Verbrennung fester wie auch flüssiger Substanzen erfolgen in der bereits beschriebenen Weise[1,2]. Als Absorptionslösung verwendet man 10 ml zirka 0,01-n Jodlösung, bei extrem niederen Arsengehalten nur 5 ml dieser Lösung. Nach vollständiger Absorption der Verbrennungsprodukte, die bei kräftigem Schütteln und Abkühlen des Kolbens nach ungefähr 10 Minuten erreicht ist, wird der Stopfen abgenommen und zusammen mit der Quarzhalterung mit dest. Wasser abgespült. Die jodhaltige Absorptionslösung wird nun quantitativ in ein 25-ml-Meßkölbchen übergespült und mit 1 ml Molybdatlösung versetzt. Nach kräftigem Umschütteln wird 1 ml Reduktionslösung hinzugegeben und anschließend das Kölbchen 10 Minuten auf einem siedenden Wasserbad erwärmt. Nach dieser Zeit wird die Lösung sofort abgekühlt und nach Auffüllen mit dest. Wasser innerhalb einer Stunde gegen einen analog angesetzten Blindwert gemessen. Die Messung von Gehalten über 10 μg wird in einem Filterphotometer durchgeführt, und zwar je nach Arsengehalt unter Verwendung der Filter Hg 691 oder Hg 578. Schichtdicke: 10 mm. Arsenmengen unter 10 μg werden zur Erzielung exakter Ergebnisse in einem Spektralphotometer bei 835 nm gemessen. Zudem wird das Endvolumen entsprechend verkleinert. In jedem Falle kann auch durch Anwendung größerer Schichtdicken eine zur Ablesung der Extinktion erforderliche Farbstärke erreicht werden. Für jeden Meßbereich (Wellenlänge und Schichtdicke) ist aber eine spezielle Eichkurve aufzunehmen.

$$\text{Berechnung: } \% \text{ As} = \frac{\text{mg As (aus der Eichkurve)} \cdot 100}{\text{mg Einwaage}}.$$

* Komplette Verbrennungskolben mit Halterung aus Quarz können von der Firma Paul Haack, Wien IX, Garnisongasse 3, bezogen werden.

Als Beispiel für die Genauigkeit und Reproduzierbarkeit wie auch die allgemeine Anwendbarkeit der Methode sind in Tabelle 1 die Analysenwerte zweier schwer aufschließbarer Arsenverbindungen angeführt.

Tabelle 1

Einwaage mg	% As ber.	% As gef.
Tetraphenyl-arsonium-chlorid		
5,656	17,89	17,97
7,703		17,87
4,140		18,03
4,372		18,07
2,975		17,90
1-(o-Arsenophenylazo)-2-naphthol-3,6-disulfosaures Na		
3,220	13,00	12,89
5,725		12,93
4,303		13,08
7,128		12,85
3,753		12,91

Die erreichbare Genauigkeit der Einzelmessung liegt bei der beschriebenen Methode bei $\pm 0{,}2\%$, also in jedem Falle unter der üblichen Fehlergrenze von $\pm 0{,}3\%$.

Den Herren Dr. *E. Abrahamczik* und Dr. *W. Huber* sei auch an dieser Stelle für wertvolle Hinweise herzlichst gedankt.

Zusammenfassung

Die sogenannte „Kolbenmethode", die Verbrennung der Substanz in einem mit Sauerstoff gefüllten Erlenmeyerkolben, konnte mit gutem Erfolg auf die mikroanalytische Schnellbestimmung von Arsen in organischen Verbindungen ausgedehnt werden. Als Haltevorrichtung für die Substanzeinwaage wurde zur Vermeidung einer Legierungsbildung Quarz an Stelle des Platins benutzt, wodurch, ganz allgemein gesehen, eine wesentlich größere Anwendungsbreite der Kolbenmethode gegeben ist. Bei nur arsenhaltigen organischen Verbindungen liefert aber auch die Verwendung sogenannten „phosphorbeständigen" Platins exakte Werte. Die Verbrennungsprodukte werden zur gleichzeitigen Oxydation von As(III) zu As(V) in verd. Jodlösung absorbiert. Zur Endbestimmung wurde die Arsenmolybdänblaureaktion in einer für Serienanalysen zweckmäßigen Form angewandt. Die Reduktion der Heteropolysäure wird mit Hydrazinsulfat durchgeführt, wobei ein Überschuß an Jod aus der Absorptionslösung nicht stört. Der errechnete mittlere Fehler einer Einzelbestimmung beträgt $\pm 0{,}2\%$.

Die Methode ist ohne weiteres im Halbmikromaßstab wie auch zur Spurenbestimmung anwendbar.

Summary

The so-called "flask method", i. e. the burning of the sample in an Erlenmeyer flask filled with oxygen, was extended successfully to the rapid microanalytical determination of arsenic in organic compounds. Quartz was used instead of platinum for holding the sample to avoid the formation of an alloy, and this precaution, in general terms, has greatly widened the field of application of the flask method. However, in the case of organic

compounds containing only arsenic, it is possible to secure precise results also by using the so-called "phosphorus-resistant" platinum. The combustion products are absorbed in diluted iodine solution to secure concurrent oxidation of As(III) to As(V). The final determination employs the arsenomolybdate blue reaction in a form that is suitable for series analyses. The heteropoly acid is reduced with hydrazine; an excess of iodine from the absorbing solution does not interfere. The calculated mean error of a single determination is $\pm$ 0.2%. The method may be used on the semimicro scale as well as for the determination of traces.

Résumé

Il a été possible d'étendre avec succès à la détermination microanalytique rapide de l'arsenic dans les combinaisons organiques la méthode «à la fiole» qui comporte une combustion de la substance dans une fiole d'Erlenmeyer remplie d'oxygène. Afin d'éviter la formation d'un alliage avec le platine, le dispositif de suspension de la prise d'essai est réalisé en quartz ce qui d'ailleurs augmente d'une façon très générale le domaine d'application de la méthode à la fiole. Toutefois pour des combinaisons organiques exclusivement arséniées il est également possible d'obtenir des résultats exacts en employant le platine dit «resistant au phosphore». Les produits de combustion sont absorbés et simultanément oxydés de As(III) en As(V) dans une solution diluée d'iode. Pour le dosage final on utilise la réaction au bleu arsénomolybdique sous une forme spécialement adaptée pour l'analyse en série. La réduction des hétéropolyacides est effectuée à l'aide de sulfate d'hydrazine; elle n'est pas gênée par la présence d'un excès d'iode provenant de la solution absorbante. L'erreur moyenne calculée pour une détermination isolée s'élève à $\pm$ 0,2%. La méthode est également applicable sans modification aussi bien dans le domaine semi-microanalytique que pour le dosage des traces.

Literatur

[1] *W. Merz*, Mikrochim. Acta [Wien] **1959**, 456.

[2] *W. Schöniger*, Mikrochim. Acta [Wien] **1955**, 123; **1956**, 869.

[3] *K. D. Fleischer, B. C. Southworth, J. H. Hodecker* und *M. M. Tuckerman*, Analyt. Chemistry **30**, 152 (1958).

[4] *L. E. Cohen* und *F. W. Czech*, Chemist-Analyst **47**, 86 (1958).

[5] *R. Belcher* und *A. M. G. Macdonald*, Talanta **1**, 185 (1958).

[6] *B. C. Southworth, J. H. Hodecker* und *K. D. Fleischer*, Analyt. Chemistry **30**, 1152 (1958).

[7] *R. Belcher, A. M. G. Macdonald* und *T. S. West*, Talanta **1**, 408 (1958).

[8] *E. Schulek* und *P. von Villecz*, Z. analyt. Chem. **76**, 81 (1929).

[9] *S. Meyer* und *O. G. Koch*, Z. analyt. Chem. **158**, 434 (1957).

[10] *G. R. Kingsley* und *R. R. Schaffert*, Analyt. Chemistry **23**, 914 (1951).

[11] *A. Crawford, J. G. Palmer* und *J. H. Wood*, Mikrochim. Acta [Wien] **1958**, 277.

[12] *M. Corner*, Analyst **84**, 41 (1959).

Mitteilungen aus chemischen Gesellschaften

The Society for Analytical Chemistry

Ordinary Meeting of the Physical Methods Group

The 65th Ordinary Meeting of the Physical Methods Group of the Society for Analytical Chemistry was held at 6.30 p. m. on Tuesday, 24th February, 1959, in the Meeting Room of the Chemical Society, Burlington House, London W. 1. The Chair was taken by the Chairman of the Section, Mr. *R. A. C. Isbell*, A. Inst. P.

The subject of the meeting was "The Analysis of Intact Samples" and the following papers were presented and discussed:

"The Use of Beta and Gamma Absorption Methods in the Analysis of Intact Samples", by *J. F. Cameron*, B. Sc. (U. K. A. E. A., Harwell).

The predominant use of gamma-absorption techniques employs the Compton scattering process for determining density. It has the advantage that it provides a non-contact measurement which can be made continuously through the walls of containers such as pipes, or tanks and is used, for example, on petroleum products, ice cream, acids, and slurries of cement, thoria and uranium. The H—C mass ratio of hydrocarbons can be determined.

Photoelectric absorption of low energy photons is a rapidly varying function of atomic number and hence can be used as an indication of mean atomic number. The scope of the technique is severely restricted, firstly by the lack of radioactive isotopes emitting low energy photons and secondly by the absorption of this radiation in the container walls. The concentration of uranyl sulphate and uranium "pulp" in aqueous solution and the sulphur and lead concentrations of hydrocarbons is thus determined.

Beta-absorption methods are used in gas analysis and smoke detection.

The accuracy of such measurements is usually limited by the statistical variations in the detector output due to the random rate of emission of radiation from the radioactive source. Choice of detector and source energy, theoretical accuracy effect of container wall, thickness, etc. are considered.

"The Use of Radioactive Isotopes in Simple X-ray Fluorescent Analysis", by *C. E. Mellish*, B. A., D. Phil. (U. K. A. E. A., Harwell).

For many applications of X-ray fluorescence spectroscopy the full performance of the conventional spectrometer is not required. In these applications it is possible to substitute a small radioactive source ($\sim$ 1 millicurie) for the X-ray tube, provided that the crystal spectrometer is also dispensed with and resolution of the fluorescent X-rays produced is performed in a proportion or scintillation counter. Results were given of the application of this simple system to such problems as the measurement of metal plate

thickness and of solution strengths. The suitability of different isotope sources for different applications was discussed.

"Analysis by Nuclear Magnetic Resonance Techniques", by *J. D. Ferrett*, M. A., D. Phil. (U. K. A. E. A., Harwell).

The phenomenon of nuclear magnetic resonance, in which responses can be obtained from nuclei that have spin, offers a technique for the analysis of intact samples of solids, liquids and gases. Equipment demands are rigorous, e. g. magnets with highly uniformed fields and electronic circuits with low noise levels. The information obtained can be both qualitative and quantitative and can be used as an aid to the elucidation of the structure of complex organic molecules.

Annual General Meeting of the Midlands Section

The fourth Annual General Meeting of the Midlands Section of the Society for Analytical Chemistry was held at 6.30 p. m. on Tuesday, March 3rd, 1959, in the Mason Theatre, The University, Edmund Street, Birmingham 3. The Chairman of the Section, Dr. *R. Belcher*, F. R. I. C., F. Inst. F., presided.

The following were elected Officers of the Section for the forthcoming year:

Chairman: Dr. *S. H. Jenkins.*

Vice-Chairman: Dr. *H. C. Smith.*

Hon. Secretary: Mr. *G. W. Cherry*, 48 George Frederick Road, Sutton Coldfield, Warwickshire.

Hon. Treasurer: Mr. *F. C. J. Poulton.*

Hon. Assistant Secretary: Mr. *R. Adkins.*

Annual General Meeting of the Society

The eighty-fifth Annual General Meeting of the Society was held on Friday, March 6th, 1959, in the Meeting Room of the Royal Society, Burlington House, London, W. 1., with the President, Dr. *J. H. Hamence*, M. Sc., F. R. I. C., in the Chair. The Financial Statement and the Report of the Council for the past year were submitted and approved, and the Auditors were appointed.

Summary of Annual Report

During the year the Society's activities have increased, and the widening scope of the methods used, particularly in industry, has received the Council's attention. To ensure adequate coverage of modern as well as classical techniques, the Council has set up a Programmes Committee to plan the main Society's meetings; Group and Section meetings remain the responsibility of Group and Section Committees. The Society has held seven meetings during the year, one before an audience of over 300 at the Royal Institution, where *T. T. Gorsuch* described his investigations into the causes of loss or gain of trace elements during the destruction of organic matter carried out for the Analytical Methods Committee: Mr. *Gorsuch* held the first research scholarship awarded by the Society's Analytical Methods Trust. Two other meetings were held jointly with other learned societies, the Association of Clinical Biochemists and the Association of Public Analysts, respectively.

An International Symposium on Microchemistry lasting 7 days was held in Birmingham in August; it was organised jointly by the Midlands Section and the Microchemistry Group, and over 400 delegates took part; there were some 60 lectures. The full proceedings are in course of publication.

The Analytical Methods Committee has expanded its activities: new work started includes a large programme on methods for determining additives in animal and poultry feeding stuffs, being undertaken as a result of a request by the Ministry of Agriculture, Fisheries and Food, preparation of methods for pesticides residues in foodstuffs and preparation of methods for chlorine in organic compounds. The Society's Joint Committee with the Pharmaceutical Society of Great Britain continues its work on methods of assay of crude drugs, the investigations being in the hands of five Panels. The Joint Committee with the Association of British Chemical Manufacturers has been disbanded, their "Recommended Methods for the Analysis of Trade Effluents" having been published in book form in July (1958).

The Microchemistry, Physical Methods and Biological Methods Groups have continued to hold very successful meetings in various parts of the country, as well as in London, and the North of England, Scottish, Western and Midlands Sections have held meetings at many places in their areas.

The Honorary Treasurer's report shows, for the first time in many years, an excess of income over expenditure in all accounts, including the Society's publications, but further consolidation is still necessary.

The year has seen the publication, besides the "Trade Effluents" book, of the "Proceedings of the Congress on Modern Analytical Chemistry in Industry", held at St. Andrews in June, 1957, and organised by the Scottish Section, and of a further Decennial Index to *The Analyst* (1946–1955). The number of subscribers to *The Analyst* and *Analytical Abstracts* again shows an increase: last year's record number of abstracts has been exceeded by nearly 200, the total published being 4412. The two journals were given new covers in January of this year.

Membership of the Society is slightly increased at 1917.

Election of Officers

The following Officers and Members of Council were elected for the forthcoming year. *President: R. C. Chirnside; Past Presidents serving on the Council: J. H. Hamence, D. W. Kent-Jones, J. R. Nicholls, K. A. Williams; Vice-Presidents: D. C. Garratt, Magnus A. Pyke, J. G. Sherratt; Honorary Treasurer: A. J. Amos; Honorary Secretary: R. E. Stuckey; Honorary Assistant Secretaries: L. Brealey* (Programmes Secretary), *S. A. Price.*

Other Members of Council: N. L. Allport, H. E. Brookes, R. A. Chalmers, W. T. Elwell, C. H. R. Gentry, J. Haslam, E. I. Johnson, G. W. C. Milner, R. F. Milton, F. C. J. Poulton, T. S. West, and *C. Whalley.*

Ex-Officio Members: J. R. Edisbury (Chairman of the North of England Section), *A. N. Harrow* (Chairman of the Scottish Section), *S. Dixon* (Chairman of the Western Section), *S. H. Jenkins* (Chairman of the Midlands Section), *F. Holmes* (Chairman of the Microchemistry Group), *R. A. C. Isbell* (Chairman of the Physical Methods Group) and *J. I. M. Jones* (Chairman of the Biological Methods Group).

Address of the Retiring President

After the Annual General Meeting, Mr. *Chirnside* took the Chair and Dr. *Hamence* delivered his Presidential Address.

Dr. *Hamence* devoted the major part of his address to the developments that had taken place over the past two years, and devoted the latter part of the address to a limited number of observations on the future course of analytical chemistry. In talking of the inner workings of the Society, he

paid tribute to the Hon. Treasurer, Dr. *Amos*, and the Hon. Secretary, Dr. *Stuckey*, who had started with him two years ago as a completely new team. Although there had been no dramatic developments during the two years – it had been a period of consolidation – all the various activities of the Society had been carefully reviewed. The improved financial situation referred to in the Annual Report – that the Society was at last self-supporting again – meant that the journals might now develop to meet the increasing demands made by analytical chemistry.

The President spoke of the Society's offices on the fourth floor of the Society of Chemical Industry's houses in Belgrave Square, and showed some photographs. He went on to mention the various Committees: much had been done to ensure representation of all regions of the British Isles on the main Committees as it was already on Council; but there were difficulties in achieving this in the two Committees whose primary tasks were the production of the journals. Sale of *The Analyst* and *Analytical Abstracts* was undoubtedly the main source of income, and much consideration had been given to them. A Committee had been set up to consider *The Analyst*, and as a first result the covers of the two journals had been re-styled and regular review articles had been started.

Another new Committee, the Programmes Committee, whose Chairman is Dr. *J. Haslam* and whose Hon. Secretary is Mr. *L. Brealey* was seeing that meetings, a vital part of the Society's life, would get the attention they required: special meetings had been held at the Royal Institution in each of the last two years, and both were highly successful. In his opinion too few original papers were now read, and he made a plea for originators of techniques to discuss them before the Society at an early stage.

The Analytical Methods Committee, a full report whose work was published every year, had been very active: he reported that the very generous response of Industry to the appeal for funds for the second three-year period permitted the work to continue on the same scale as before. Several important projects of this Committee's Sub-Committees and Panels were nearing completion, namely reports of the Vitamin-E Panel and of the Joint Committee with the Pharmaceutical Society. A separate Sub-Committee was being set up and additional staff engaged to undertake the work of publishing standard methods, which the Society was pledged to do by its appeal to Industry.

The annual Conference of Group and Section Secretaries was actively considering the Section boundaries, as many problems arose owing to the difficulties of cross-country travel. The functions of the Groups had also been reviewed. One Group, which at one time had rather regarded its useful work as having finished, might, he said, find bio-assays beginning to play an increasingly important part in the determination of pesticides residues and growth substances.

Heartening tributes had been paid to analytical chemistry by Dr. *J. Craik* at the St. Andrews Congress and Professor *Stacey* at the Birmingham Symposium, and the Meldola Medal for 1957 had been awarded for the first time for process in analytical chemistry to Dr. *T. S. West*. The papers read at the two Congresses showed the great strides made in techniques, much instrumentation having been introduced in recent years: he hoped classical methods would not be neglected in consequence, as they were still important. Gas chromatography was replacing many laborious procedures, and the Analytical Methods Committee was alive to this: the Essential Oils Sub-Committee was applying it to its problems.

Automation had led to many new discoveries; for example, the fact that the oxygen content of river water receiving sewage effluent varies with the time of day, a fact that would have gone unnoticed without automatic recording equipment.

He hoped food chemistry would not become too neglected as a result of the increasing applications of analysis elsewhere. The technique described by Professor *Tiselius* and referred to by Dr. *Synge* at St. Andrews of separating relatively large microscopical particles between two solvent phases might well prove of importance in separating the components of a mixed foodstuff.

The President ended by reporting that the Society was healthy and going from strength to strength. He quoted Browning:

"Grow old along with me,
The best is yet to be."

Anniversary Dinner

In the evening following the Annual General Meeting, a Dinner to celebrate the eighty-fifth anniversary of the Society was held, by kind permission of the Prime Warden, Wardens and Court of Assistants of the Worshipful Company of Fishmongers, at Fishmongers' Hall, London Bridge. The members and guest, numbering 141, were received by the President, Dr. *J. H. Hamence*, M. Sc., F. R. I. C., and Mrs. *Hamence*. The President afterwards took the Chair at the Dinner.

The Guests of the Society and of the President included Sir *Henry Melville*, K. C. B., D. Sc., F. R. S. (Secretary of the Department of Scientific and Industrial Research) and Lady *Melville*; Professor Sir *Charles Dodds*, M. V. O., D. Sc., Ph. D., M. D., Hon. Sc. D., F. R. C. P., F. R. I. C., F. R. S. E., F. R. S. (Courtauld Professor of Biochemistry, University of London) and Lady *Dodds*; Professor *H. J. Emeléus*, Ph. D., D. Sc., A. R. C. S., F. R. I. C., F. R. S. (President of The Chemical Society) and Mrs. *Emeléus*; *D. W. Kent-Jones*, B. Sc., Ph. D., F. R. I. C. (Acting President of the Royal Institute of Chemistry) and Mrs. *Kent-Jones*; *A. K. Mills*, B. Sc., Ph. D. (Vice-President of the Society of Chemical Industry) and Mrs. *Mills*; *H. E. Monk*, B. Sc., M. Inst. S. P., F. R. I. C. (President of the Association of Public Analysts); The Honorable Mr. *Justice Lloyd-Jacob*, M. A., D. C. L. (Chairman of the Analytical Methods Trust) and Lady *Lloyd-Jacob*; and *F. A. Pester* (representing the Worshipful Company of Fishmongers) and Mrs. *Pester*.

The Loyal Toast was proposed by the President.

Sir *Harry Melville* proposed the Toast of the Society. He felt that the Society's founder members, the original Public Analysts, would be surprised at the modern members, some practically physicists. The Society had ranged from nuclear magnetic resonance to clinical biochemistry at its meetings during the year. The future of analytical chemistry was bound up with rapid automatic methods, and the Society was leading the way through its recent Congress and Symposium. The Toast of the Society was coupled with the name of the President.

Dr. *Hamence* replied, saying that he had been heartened by the way both Dr. *Craik* and Professor *Stacey* had paid tribute to analytical chemistry in introducing the two Congresses. The subjects covered at them had ranged from a study of the reactions in the surface layers of metals in an atomic pile to the production of better ice-cream. They were a credit to the younger generation, by whose enthusiasm and efforts they were organised.

Mr. *Chirnside* proposed the Toast of the Guests. Sir *Harry Melville*'s distinguished career had embraced two periods of professional work, and he was a Meldola Medallist of long standing: besides this he was known as a conductor of choral music. Professor *Emeléus* was President of the oldest Chemical Society in the world: our Society was proud of being the second oldest. The presence at this dinner of these two eminent academic chemists contrasted completely with the attitude of academic chemists in 1875, who considered Public Analysts as being outside the pale. Dr. *Mills* represented the Society of Chemical Industry in the absence of Sir *Robert Robinson*, and he thanked that Society for their benevolent landlordship. Dr. *Kent-Jones*, who had been to Anniversary Dinners before, both as President of the Society and as President of the Royal Insitute of Chemistry, was personally most welcome, although the reason why he was Acting President of the Institute was a matter all deeply regretted. Mr. *Monk*, here as President of the Association of Public Analysts, was another old friend: it was of interest that one of the names suggested in 1875 for the Society had been "Association of Public Analysts". Sir *George Lloyd-Jacob* was an Honorary Member and Chairman of the Analytical Methods Trust, and had delivered a memorable Bernard Dyer Memorial Lecture in 1952. Sir *Charles Dodds* had had a distinguished career in biochemistry, and, indeed, had broadcast only the previous Friday on "Laboratories behind the Doctor", telling of what the doctor and his patients owed to modern analytical methods such as flame photometry and electrophoresis. Finally, Mr. *Chirnside* came to the Ladies, without whom the atmosphere on an occasion such as this dinner would be rather lost, who let us go to these Congresses, who were appearing at the benches of analytical laboratories in growing numbers, and whose influence was everywhere very good indeed. The Toast of the Guests was coupled with the name of Sir *Charles Dodds*.

Sir *Charles Dodds*, in reply, said that it was quite true that medicine would not be in the position it was in today without analytical chemistry. He said that Dr. *Kent-Jones*'s work provided another example of change: in the Middle Ages it was a crime to put chalk in flour; now the reverse was true, and a miller could be heavily fined if he failed to put in the statutory amount.

The President concluded the proceedings by calling upon Mr. *Chirnside*, the new President, who, he said, had done much to persuade Council just after the war of the extreme importance of the new physical and biological methods of analysis and so had helped give the Society its "New Look", and who was responsible for the Society's successful venture, *Analytical Abstracts*, and invested him with the Presidential Badge, wishing him a successful term of office. Mr. *Chirnside* expressed his pleasure at the honour, and presented Dr. *Hamence* with a replica of the Society's badge to wear as Past President.

Joint Meeting

A Joint Meeting of the Midlands Section and the Physical Methods Group of the Society for Analytical Chemistry was held at 6.30 p. m. on Friday, March 20th, 1959, in the Mason Theatre, The University, Edmund Street, Birmingham 3. The Chair was taken by the Chairman of the Physical Methods Group, Mr. *R. A. C. Isbell*, A. Inst. P.

The Meeting was preceded at 2.15 p. m. by a visit to the Research Laboratories of Albright & Wilson, Ltd., Trinity Street, Langley, Oldbury.

The subject of the meeting was "X-Ray Fluorescence" and the following papers were presented and discussed:

"Instrumental Developments in X-ray Fluorescence Spectroscopy", by *J. R. Stansfield*, M. A., F. Inst. P. (Hilger & Watts Ltd.).

Analysis by X-ray fluorescence was both accurate and rapid and had been applied to the determination of elements in alloys, powders, liquids and other materials.

An instrument for such work included a powerful source of X-rays to irradiate the sample, a crystal spectrometer, and a detector to measure the intensity of the radiation emitted by the sample at each characteristic wavelength. These various components and the many different forms which they could take were discussed, and illustrated by descriptions of automatic and manual instruments.

"Some Applications of X-ray Spectrography", by *H. I. Shalgosky*, B. Sc., A. R. I. C. (U. K. A. E. A., Woolwich).

The extremely rapid determinations which were possible using X-ray spectrography, e. g. the determination of chromium, nickel, manganese, and titanium in stainless steels were compared with determinations made on samples having variable compositions, e. g. the determination of uranium in ores. The use of the technique for determinations at the p. p. m. level was also described.

Ordinary Meeting of the Society

An Ordinary Meeting of the Society was held at 7 p. m. on Wednesday, April 1st, 1959, in the Meeting Room of The Chemical Society, Burlington House, Piccadilly, London, W. 1. The Chair was taken by the President, Mr. *R. C. Chirnside*, F. R. I. C.

The following papers were presented and discussed:

"A Modified Hydroxamic Acid Method for the Estimation of Total Esterified Fatty Acids in Plasma", by *D. M. Morgan* and *K. J. Kingsbury*, M. B., B. S., Ph. D. (Surgical Unit, St. Mary's Hospital, W. 2.).

A colorimetric procedure was presented for the estimation of esterified fatty acids in plasma based on the formation of hydroxamic acids and their reaction with ferric chloride to give a coloured complex. The method, which was adapted from published methods, had few manipulative steps, required no special apparatus, and enabled a large number of estimations to be performed by one person.

"The Determination of Small Amounts of Alpha Picoline in Pyridine by a Solution Temperature Method", by *K. A. Adey*, B. Sc., F. R. I. C. (The Midland Tar Distillers Ltd., Four Ashes, nr. Wolverhampton) and *J. D. Cox*, B. Sc., Ph. D., A. R. C. S. (National Chemical Laboratory, D. S. I. R. Teddington).

Concentrations up to 2 per cent of α-picoline in pyridine might be determined with an uncertainty of ca. $\pm$ 0.1%, by measuring the lower solution temperature of a mixture containing the two bases, water and potassium chloride in specified proportions. With the assumption that the only impurities in "pure pyridine (99% minimum)", as defined by the British Standards Specification for this grade, were α-picoline and water, the pyridine content could be found by difference. The method described was thus an alternative

to that based on the clearing-temperature of a perchlorate solution, which had been adopted in the Specification.

"The Separation of Copper, Cobalt, and Nickel", by *W. D. Duffield* (26 Park Crescent, London, W. 1).

Copper, Cobalt, and Nickel were extracted from solution at p_H 8.0 with a chloroform solution of 8-hydroxyquinoline. This removed them from large quantities of Ca, Mg, Na, K, etc., the extracted oxinates produced ash of low bulk which might be re-dissolved in a minimal volume and applied quantitatively to a sheet of chromatography paper.

After chromatographic separation, the zones containing the respective metal salts were located with Rubeanic acid. The appropriate areas were then cut out, ashed, and metals determined colorimetrically.

"The Additive Effect of Substituent Groupings in the Chromatographic Behaviour of Phenoxyacetic Acids", by *L. S. Bark*, B. Sc., F. R. I. C., and *R. J. T. Graham*, B. Sc. (Derby and District College of Technology, Derby).

Series of chlorinated and methylated phenoxyacetic acids were chromatographed by an ascending technique under standardised conditions, of temperature, flow rate, etc., so that changes in R_f value of compounds in the series were caused mainly by the change in the number of substituent groupings introduced into the parent phenoxyacetic acid nucleus.

The effect of variation of p_H of R_f was also briefly studied.

The Eleventh Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy

will be held at the Penn-Sheraton Hotel in Pittsburgh, Pennsylvania, U. S. A., from February 29 through March 4, 1960.

Original papers are invited on all phases of analytical chemistry, spectroscopy, and nucleonics applied to analysis. The final date for receipt of abstracts is October 15, 1959. Two abstracts should be submitted in triplicate. The first abstract should be limited to 150 words to be printed in the program. The second abstract should be of approximately 500 words to help the Program Committee evaluate and classify the paper. A letter sent with the abstracts should list the names of authors, laboratory in which the work was done, and the current addresses of the authors. All correspondence should be addressed to:

James E. Paterson, Program Chairman,
The Eleventh Annual Pittsburgh Conference
Jones & Laughlin Steel Corporation
Graham Research Laboratory,
Pittsburgh 30, Pennsylvania.

In addition to the program of technical papers, there will be an exhibition of the newest instrumentation for analysis. More than seventy-five companies will display instruments, chemicals, and equipment.

Groupe de la chimie analytique de la Société de chimie industrielle

Séance du Jeudi 8 Janvier 1959 sous la présidence de Monsieur le Professeur *G. Chaudron*, Membre de l'Institut.

La séance est ouverte à 17 h 30.

Monsieur *Clément Duval* commente et présente un film de 35 mm, parlant et en couleurs, intitulé: «*Parfums de France*», d'une durée de 50 minutes et comprenant les quatre parties: culture et cueillette des fleurs, extraction des principes odorants, préparation de produits de synthèse, réalisation d'un parfum et fabrique de la verrerie.

Dans une deuxième partie, Monsieur *Clément Duval* expose un résumé des travaux effectués en 1958 au laboratoire de recherches micro-analytiques de l'E. N. S. C. P. en associant la spectrophotométrie infra-rouge et la thermogravimétrie. C'est ainsi qu'il parle de l'utilisation des courbes dressées en 1941 avec *J. Lecomte* concernant la fréquence de la vibration triplement dégénérée des groupes XO_4 en fonction du poids atomique de l'oscillateur X. Il décrit un nouveau cas d'isomérie relatif à la cobaltiammine $Co(NO_2)_3(NH_3)_3$; il montre que les sels dits d'uranyle ne contiennent pas le cation UO_2^{++}, que le chlorure de formyle n'existe pas dans le mélange CO + HCl, que la surcharge en fer du sulfate de baryum précipité est dûe à un produit d'insertion (avec *Jeannin*), que l'alun de chrome est un complexe dans lequel figurent trois sortes de molécules d'eau (avec Melle *Harmelin*), que les sélénites ont un spectre d'absorption infrarouge concordant avec le spectre Raman (avec Melle *Rocchiccioli*) qu'il existe quatre sortes d'hydroxydes minéraux (avec Madame *Cabannes*), que l'on peut déceler par chromatographie ascendante sur papier les anions minéraux contenant du soufre et les caractériser par infrarouge dans une microgoutte de solution (avec Madame *Garnier*), que l'on peut déceler la nature des produits formés par réaction à l'état solide entre l'oxylithe et les oxydes minéraux (avec Madame *Viltange*), étudier la structure des chromates et des halogénochromates (avec Madame *Dupuis*) et poursuivre l'étude des étalons utilisés en analyse volumétrique (avec Melles *Servigne* et *Wadier*).

La séance est levée à 19 heures.

Compte-rendu succint de la séance du 5 Février 1959.

Le Président *Roger*, après avoir annoncé des nouvelles concernant la vie du Groupe, donne la parole à M. *Ch. Dozinel*, sur la «Rationalisation en Analyse Chimique».

La rationalisation des méthodes est devenue une nécessité, et même certains procédés éprouvés peuvent encore y gagner (façon de titrer un acide fort, dosage du Mn par colorimétrie au persulfate d'ammonium en présence de nitrate d'argent).

Malheureusement la plupart des procédés analytiques sont plus complexes. Il faut considérer exactitude, précision, simplicité, rapidité et bas prix de revient.

M. *Dozinel*, qui a visité un grand nombre de laboratoires a constaté que le principal obstacle à la rationalisation n'était pas d'ordre technique, mais d'ordre psychologique.

Les cycles d'analyses entre différents laboratoires montrent que partout où la normalisation intervient, les écarts constatés auparavant entre eux diminuent très largement. Mais des progrès restent à faire.

Colloquium Spectroscopicum Internationale VIII

Das in der Zeit vom 14. bis 19. September 1959 in Luzern stattfindende Kolloquium umfaßt folgende Hauptthemen:

Emissionsspektroskopie — Fluoreszenzspektroskopie — Massenspektroskopie.

Jede Diskussionssitzung wird mit einem Hauptvortrag eingeleitet werden. Die Referenten und ihre Themen sind:

W. Lochte-Holtgreven, „Spektroskopische Diagnostik in der Physik heißer Plasmen".

H. C. van de Hulst, „Investigations of the Interstellar Gas by Optical and Radio-Spectroscopy".

A. Hans, „Développements nouveaux en quantométrie".

R. Mavrodineanu, „Quelques considérations sur l'analyse spectrale quantitative par la flamme".

E. Schumacher, „Probleme der Massenspektroskopie".

E. Lüscher, „Some Problems of the Spectroscopy in the Schumann and Lyman Region".

An das Kolloquium wird wie üblich eine Instrumentenausstellung angegliedert, die einen Überblick über moderne Geräte für die Spektroskopie ermöglicht. Auch werden Exkursionen in industrielle Anlagen und wissenschaftliche Institute der Schweiz durchgeführt.

Der Tagungsbeitrag für ordentliche Teilnehmer beträgt sfr 35,—, für Begleitpersonen sfr 20,—.

Weitere Auskünfte können beim wissenschaftlichen Beirat des Kolloquiums, Herrn Prof. Dipl.-Ing. *H. Svejda*, Wien IX, Währinger Straße 59, erfragt werden.

Buchbesprechung

Histochemische Methoden, 15. und 16. Lieferung (1958). Eine Sammlung, herausgegeben von *W. Lipp*. Jährlich etwa 4 Lieferungen. München: R. Oldenbourg. 6 Lieferungen DM 30,—, Einzellieferung DM 6,—.

In sinngemäßer Weiterführung der in den letzten Lieferungen beschriebenen histochemischen Methoden für den Nachweis der Nukleinsäuren wird in der 15. Lieferung eine Übersicht über die derzeit bestehenden Möglichkeiten, Nukleoproteide durch den Nachweis der einzelnen Komponenten zu erkennen, gegeben. Dieses Heft enthält außerdem noch einen allgemeinen Abschnitt über die Chemie der Nukleoproteide und Nukleinsäuren sowie eine für die praktische Laboratoriumsarbeit sehr wichtige Darstellung der bekannten Verfahren zur Fixierung von Nukleinsäuren und Nukleoproteiden in Geweben.

Die 16. Lieferung beinhaltet die Vorschriften zur Ausführung der Feulgen-Naphthoesäurehydrazid-Reaktion, der Turchini-Reaktion, deren Zuverlässigkeit für den gleichzeitigen Nachweis von Desoxyribonukleinsäure und Ribonukleinsäure im Gewebe noch umstritten ist, sowie Angaben für den Nachweis von Esterphosphatiden mit Hilfe von Chromierungsverfahren und schließlich Angaben für die Extraktion von Lipiden aus Gewebe mit Hilfe von Pyridin.

W. Stöckl-Wien

Berichtigung

Im Beitrag „Emissionsspektrographische Doppelbogenanalyse leichtflüssiger Spurenelemente in Graphiten" von *I. Janda* und *E. Schroll* (diese Zeitschrift 1959, Heft 3, S. 389) ist die Abb. 1 auf Seite 390 um 90° gegen den Uhrzeigersinn zu drehen.

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